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Plastics

Dealing with the Manufacture, Uses and Potentialities of Plastic Materials

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Building Plastics

WITH this issue the series of articles written by Mr. George Fejér on the subject of Plastic Building Components come to an end. The method of his attack on this extremely important and intriguing subject has been as illuminating as it has been novel.

Mr. Fejér's first object was to show to the plastics industry what the builder's present problems and manner of working are, and to show the building industry something of what the plastics industry can offer. Not that he professes to be anything of a plastics technologist. Indeed, beyond a fairly wide practical experience of organic glasses he freely admits that most of the modern industrial mouldings, extrusions, injections and laminations he has encountered have been in this office. His suggestions, as we have already indicated, are guides and are not necessarily true examples.

With this we need not grumble if we learn something from his articles. It stands out with staggering clearness that, quite apart from post-war construction, the building industry is an enormous buyer of raw and finished material. It is also clear how great a part the plastics industry can play in supplying some of its needs.

On going to press we have received a further communication from the author which he submits as a " tail-piece " to his last paragraph on " Technical Recommendations."

" The proper way of using plastic components," he states, " is nearly as important as any of the general characteristics or quality of the manufacture. The question of quality has to be outlined rather strictly, and a number of small-scale preliminary tests are inevitable. The code of practice of fixing and maintenance may require tools and methods unfamiliar to the builders, and certain modifications of the original design might be necessary on that account alone.

" The building world has been overwhelmed in the past by the amount of well-planned technical information issued by modern industries; and it seems, therefore, necessary that new products can be launched only by giving the builders and architects at least the elementary facts about it in a well-planned manner.

" The use of every component which goes into a building has to be approved by the owner, specified by the architect, and understood by the contractors, down to the building operatives who carry out the actual fixing. The technical guidance to appeal to all these individuals is quite essential.

" The above points are a few of those considerations which tend to modify designs, or to show the impracticability of otherwise good ' ideas.'

"Whether plastics will take their share in post-war building depends largely on the policy which is pursued now. It appears to be quite within the scope of plastics to produce a few good components for huts, ships, hospitals and factory buildings now, and to prepare the production of more elaborate components for post-war buildings, interior decoration and export."

Welding Plastics

THOSE who have followed the variety of papers in this journal on films and adhesives must have recollected how widespread is this process of sticking one thing to another in order to get a strong joint. The stuff that sticks is almost invariably an organic compound, ranging in history from animal and fish glues, natural gums, casein, celluloid and rubber solutions to the modern synthetic variety of phenolic and urea resins and the numerous polymers. How successful these latter compounds have been, with their great strength and flexibility and their resistance to moisture and fungus, so important in retaining that strength, we have all been aware in the past few years. They have driven a deep wedge in a market that was the prerogative of natural materials.

Indeed, of the thermosetting type hardened by heat plus the aid of an acid catalyst, it can be claimed with good reason that the resin bond is often stronger than the materials it holds together. On the other hand, use of the thermoplastic adhesives in solvent form cannot normally produce a very strong structure, although the result may be what is called "satisfactory for all purposes." The trouble lies, naturally enough, in the fact that a solvent is used and the solvent must evaporate.

So much for the jointing of the older materials of construction. When we consider the jointing of plastics the problem is often even more difficult. The cementing of two pieces of cured thermosetting resin is exceptionally difficult and it is only recently that claims have been made of the solving of the problem, using a thermosetting resin in solution. The cementing of two pieces of thermoplastic resin is normally carried out with solutions of the same or similar resin, but the process has the drawbacks already mentioned. The possibility of cementing polymers with monomers, that is, the raw materials from which the polymers are made, is interesting, although the technique may prove somewhat difficult.

In view of all this, there has always been a need for a process of joining two pieces of plastic by a method analogous to the welding of metals. In fact, it is no exaggeration to say that certain developments in plastics have hitherto been held up because of this lack. Obviously, the welding of the two pieces of cured thermosetting resin is impossible by heating. But two pieces of thermoplastic resin can now be heated and caused to flow together, so that, on trimming and polishing, the jointing line is invisible or very nearly so. The two pieces have virtually become one. The whole is as strong as each piece.

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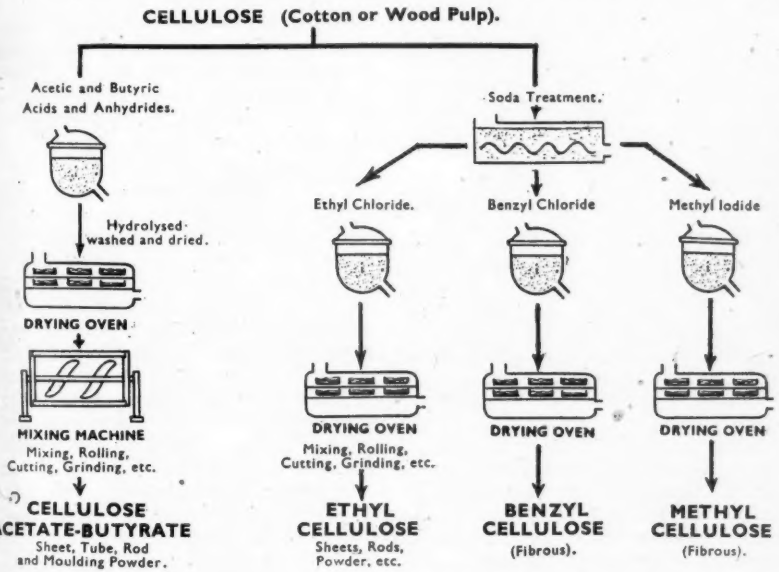
PLASTICS: *Their Origin and Formation*

3.—CELLULOSE PLASTICS (Contd.)

THE number of possible chemical derivatives of cellulose is very great although it is limited in industrial production. In the May issue we described the production of the three best-known cellulose plastics:—Celluloid, cellulose acetate and regenerated viscose film. We continue with some of the lesser-known varieties.

NOTE.—Cellulose nitrate, acetate and aceto-butyrate materials are known chemically as esters, that is, compounds which are formed by the interaction between alcohols (cellulose with its many OH groups may be so considered) and acids. The group which includes ethyl, benzyl and methyl celluloses is called the ether group, compounds formed by the interaction between alcohols and substances like ethyl chloride.



Cellulose Acetate-Butyrate, which in appearance is exactly like cellulose acetate, is stated to possess certain advantages over the latter in being more water-resistant. It possesses better injection moulding characteristics than the acetate and mouldings made from it are freer from distortion. Tensile strength and other mechanical properties are about the same. Made only in the U.S.A. **Trade Name.**—Tenite II (U.S.A.).

Ethyl Cellulose. The film and sheet are excellent electrical insulating materials and possess great toughness at low temperatures. Water absorption and strength are about the same as cellulose acetate. It is considerably lighter than the acetate.

Uses.—Foils, wire insulation, rigid containers, extruded strips for rattan furniture, injection mouldings.

Trade Names.—There are three British manufacturers of this material. Ethocel (U.S.A.).

Benzyl Cellulose. So far as is known, produced only in Great Britain for use in lacquers. Other suggested uses are as foils, mouldings, etc.

Methyl Cellulose. Not a moulding plastic. "Soluble" in water, is used as a base for sizing agents, face creams, medical preparations, etc.

PLASTICS VERSUS LEATHER

By Haydon K. Wood

SHORTAGE of sole leather and upper leather occasioned by the ever-growing demands of the fighting services is recognized as a golden opportunity for alternative materials, materials, incidentally, which deserve a more generous description than the ubiquitous "substitute." Prominent among the materials on trial to-day are plastics, particularly the new vinyl resins. It was reported only a few weeks ago that the Quartermaster Corps of the U.S. Army has for some time been experimenting with plastic soles on service footwear and that "at this moment on a number of soldiers' feet are shoes with soles of a vinyl plastic material, laminated to leather, being worn in tests to determine the suitability of the material." According to the informative "Women's Wear Daily" (U.S.A.) "it is understood the testing will not be complete for several months, but that footwear already worn for about three months still have the soles unworn. The plastic, said to be several times tougher than leather, has been developed in several degrees of flexibility."

Claims for Plastic Sheet

It is claimed that the use of a plastic bottom for the sole leather not only improves the wearing and water-resisting properties but also eliminates any necessity for bottom finishing. This is usually carried out with a liquid pigment stain applied to the leather with a brush and finished off by mechanical brushing at 300 to 750 r.p.m. The plastic sheeting made to adhere to the lightweight sole leather can be coloured and printed as desired and may be produced so as to improve the attractiveness of the sole.

Plastics, either in the form of uniform cut-out from sheets or as ingredients of special compositions, are being tried out in Germany for the insoles of shoes. The insole or innersole forms the inside of the bottom of the shoe and conceals stitching, nails, etc., used in attaching the sole to the upper. The insole is usually made of leather, but may also consist of composition, fibreboard, pasteboard, felt or cork, etc.

Recent American Technique

In these American experiments the vinyl resin sheet form is cemented on to the leather half sole, presumably using heat and pressure. Whilst little headway has been made in this country on these same lines there are one or two concerns producing laminated sole leather utilizing various rubber and pyroxylin cements. This laminated material is regarded somewhat disdainfully by what might be termed the legitimate sole leather tanners, but it is confessed that there is now a very great opportunity for the laminated sole owing to the fact that all the heavier bends are ear-marked for military purposes and more and more of the lighter grades have to be used. These are not themselves thick enough or strong enough for anything but the lightest women's shoes and the only means of utilizing them on a large scale for heavier footwear is by laminating them. A good deal of interest is being taken in the acrylic adhesives and also some of the newly developed vinyl compounds. One suggestion prompted by the experiments in America is that thin sheets of a suitable vinyl resin should be used to interleave the laminates and so build up a reinforced material.

In the cemented process of shoemaking, which is a method whereby the upper is cemented to the sole instead of being attached by stitching, nailing, or pegging, plastic adhesives, either in liquid or sheet form, are already of very great importance. E. I. Du Pont de Nemours and Co., Inc., have for some years now been producing a specially developed pyroxylin cement for the cementing

process and the United Shoe Machinery Corporation produces a good deal of plant for automatic cementing. To-day, modern methods of cementing are so advanced that footwear can be produced faster by this method than the normal one.

Application of "Vinyl" Resins

Some time ago a new vinyl resin sheeting material was introduced in America for use as a tip and foxing material. For the benefit of those not actively engaged in the shoe trade it may be stated that the tip is a piece of leather covering the forepart of the vamp of a shoe to the toe; foxing is the back part of a shoe upper from shank to heel. Vinyl resin on a coutil base has also been used as an alternative to patent leather which itself is produced by coating a linseed oil mixture, subsequently oxidized, on light hide or calf. A recent issue of "Women's Wear Daily" stated: "A year's wear tests have shown that it does not check or crease under ordinary wear conditions, that the shoes can be washed with mild soap and water, and polished if desired, with any neutral wax." In a statement to the Press the managing director of Rudolph Loewenstein Corp., U.S.A., manufacturers of this "patent leather," said: "It was thought that the greatest possibilities lay in the development of a plastic shoe material that would not depend primarily on style acceptance, but rather on functional and economic suitability. Accordingly, the Loewenstein firm started by trying to develop a material that might improve on the least satisfactory leather, patent. We were not convinced that the breathing quality of leather, its porosity, was the major reason why leather should be more comfortable in shoes than plastic materials. It seemed possible that the ability of a shoe to absorb moisture, such as perspiration, might be the answer. So we set out to make sure that patent plastic shoes could, if necessary, absorb perspiration."

The Waterproofing of Leather

During 1941 experiments were carried out in Great Britain and America to produce a commercially useful waterproof sole leather for service footwear. Emulsions of natural waxes; solvent solutions of synthetic waxes, e.g., chlorinated paraffin wax; Aroclors, etc., have all been tried with varying success and also attempts have been made to employ urea-formaldehyde resins. So far these latter experiments have not met with great success, but the writer considers that they offer promise if developed on specialized lines. Aqueous solutions of urea-formaldehyde resins which can be polymerized or hardened by weak solutions of organic acids and emulsions of freshly polymerized resins are of interest as possible means of improving the water resistance of sole leather. This could be effected by a simple drumming process which would not seriously add to the processing cost. The resin would, of course, have to be plasticized so as to produce a non-brittle, flexible resin. Another suggestion is that polyvinyl chloride could be calendered on to sole leather to give it an added surface which would enhance its wearing and water-resisting properties. Some of the new plastics produced from petroleum products are also receiving attention as possible reinforcements.

The Necessity for Research by British Workers

It is realized that although to-day there is little opportunity for British plastics manufacturers to develop materials capable of improving leather, or replacing it, owing to the strain already placed on the industry by the ever-increasing demands of the vital war industries, at the same time some research seems indicated as an insurance when normality returns and fresh markets have to be opened. The fact should also be borne in mind that our imports of hides and skins from Eastern sources are rapidly shrinking owing to the advance of the Japanese, and the shoe industry may have to be granted some priority of plastic supplies to make up for a percentage of the deficiency. All developments, political and economic, point to the necessity of careful examination by the British leather industry of the new materials.

LIGNIN—A Plastic from Wood

There has been but little reasoned and collected information regarding Lignin and its uses as a plastic. The following notes give a résumé of our present knowledge of a material of great potentialities

By JULIUS GRANT, M.Sc., Ph.D.

THE term "plastic" is used to cover a wide range of materials of very different nature, but having in common the property of mouldability. The terms of this definition mean that natural as well as synthetic substances are brought into this single category of plastics, and it also leaves the door open for the addition of new substances which need possess only the one necessary property in order to qualify for inclusion.

The subject of this article, lignin, completely fits in with this definition. It is a natural substance and one which has been known for many years, but it is only comparatively recently that its potential value as a plastic has been realized. This is because difficulties were experienced formerly in isolating it in such a condition that it could be used as a plastic, but it may safely be stated that many of these troubles have now been overcome, and that lignin plastics are now an accomplished fact. It should, however, also be made clear that this branch of the industry is still very much in its infancy, and that the manufacturing details available are scanty and to some extent masked by the patent literature and usual "camouflage" associated with trade secrets. Certain outstanding facts are, however, evident, and it is felt that a summary of these may prove of interest as an indication of the future possibilities of this new material.

Lignin is a constituent of many plants, but it is more abundant in wood than in most of the other plant substances. Table 1 (J. Grant[1] and J. W. Bowen[2]) indicates the relative compositions of some common plants and illustrates this point.

TABLE 1[1,2]
Composition of Some Plant Materials

Plant Material.	Cellulose.	Lignin.	Pentosans.
Bagasse ...	60.2	21.7	29.1
Cereal Straws—			
Barley ...	48.6	16.4	31.9
Oats ...	43.8	18.5	22.8
Rice ...	45.5	10.9	21.5
Rye ...	36.3	11.3	20.4
Wheat ...	56.7	16.6	28.4
Cornstalks ...	38.4	34.3	27.6
Cotton ...	91.2	—	—
Flax ...	92.0	4.0	2.0
Hemp ...	79.3	5.2	5.5
Jute ...	74.9	11.7	18.1
Linseed Straw	53.8	23.3	17.1
Ramie ...	85.0	1.0	2.0
Sisal ...	77.0	6.0	13.0
Wood—			
Aspen (poplar)	62.1	26.5	17.6
Beech ...	67.1	22.5	24.9
Birch ...	64.2	19.6	27.1
Jack pine	57.6	33.6	12.3
Pine ...	60.5	26.4	11.0
Spruce ...	60.9	30.2	12.6

The function of lignin in the plant structure is principally as a binding agent, holding the cell walls and fibres together. In this respect, therefore, it is used as a plastic by Nature, and it is not surprising that attempts have been made by man to turn this same property to practical use for his own ends. It should be made clear at this stage that there is good reason to believe that the lignin varies somewhat in character according to the particular function it fulfils in the plant. Thus lignin which forms part of the cell-wall probably differs from the lignin which is situated between the cell-walls (intercellular

lignin). The basis of this difference is probably the state of combination of the lignin with other substances, rather than variations in its own actual chemical composition. Thus while some types of lignin (e.g., the intercellular lignin) are present in the "free" state, other lignin (e.g., from the cell-walls) may be loosely combined, particularly with carbohydrates or cellulose (ligno-cellulose). This point of distinction is an important one, because, as we shall see later, it has a bearing on the properties of the lignin obtained by different methods of isolation.

Relationship Between Lignin and Wood Processing

At this stage it may be mentioned that the isolation of lignin is to a great extent intimately bound up with the processing of wood for the manufacture of cellulose pulp. It is obvious that this should be so, since the object of the cellulose pulp manufacturer (whether he is making the raw material for rayon or for paper) is the isolation of the cellulose fibres in as pure a state as possible; he must, therefore, loosen the lignin which binds the fibres together, and then remove it or destroy it so as to purify the fibres. In this sense, therefore, lignin may be obtained as a by-product, a matter of some importance from the point of view of production economics. It has been calculated, in fact, that some 1,500,000 tons of dry lignin substance are rejected into streams and sewers each year as waste liquors from wood pulp mills.

There are two basic methods of obtaining cellulose from plant materials, and from wood in particular, namely, the acid (sulphite) process and the alkaline (caustic soda or sodium sulphide) process (see J. Grant[1,3]). A. L. M. Bixler[4] has shown that while the alkaline liquors exert a rapid initial attack on the intercellular lignin and subsequently on the cell-wall lignin, the sulphite liquor appears to enter the structure of the plant via the fibre lumen; it then dissolves the lignin in the cell-walls and in the middle lamella, and, of course, it also hydrolyses the simpler carbohydrates present. The results of the action of these two types of reagent on the lignin are also correspondingly different. Thus it is probable that the alkaline reagents have little decomposing effect, but act primarily as solvents, forming possibly loose combinations of alkali and lignin. The sulphite liquor, on the other hand, is known with more certainty to form lignosulphonic acids, and these account for many of the numerous and varied properties of these waste liquors (J. Grant[3]). It is evident, therefore, that liquors of both types may be regarded as potential sources of lignin, but that the alkaline liquors are the more promising, because the lignin is relatively little changed in character; it can, in fact, be precipitated by acid from such liquors, and this is the basis of one of the most important of the methods of isolating it on the industrial scale (see below).

Structures in Wood

In this connection Bixler's experiments are both interesting and instructive. He digested cross-sections of spruce wood, 0.02 mm. thick, with the various liquors under varying conditions of temperature, concentration and time, and he was thus able to differentiate three main structural types and two sub-divisions, viz.:

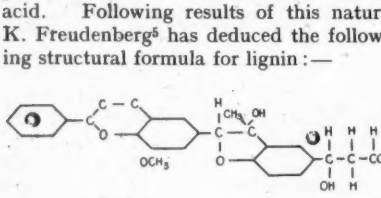
(1) Intercellular matter—mostly lignin, with some hemicellulose.
(2) Cambial walls—mostly cellulose.
(3) Secondary walls, comprising
  (a) Outer walls—mostly lignin.
  (b) Inner walls — mostly cellulose with a little lignin.

The alkaline liquors were found to be selective and fairly good solvents for the lignified structures; whilst the sulphite liquor is much less selective in its action, and attacks both (1) and (3b) at the same rate, although much less rapidly than does the alkaline reagent.

It is also of further interest to consider the actual chemical structure of lignin, since this, too, has a bearing on the methods of isolating it and on its properties. This structure has not yet been fully established, but a number of facts are known for certain. Thus it has been shown that lignin is an aromatic sub-

stance, consisting of a benzene ring to which is attached a highly reactive side-chain containing 3 carbon atoms, i.e., R-C-C-C. An interesting point is that the portion of the molecule represented by R-C- is phenolic in character, and is very closely related to vanillin, the flavouring material obtained from natural pods made synthetically from oil of cloves; vanillin is, in fact, at present being prepared on a commercial scale from the waste liquors from the sulphite cellulose process[3,13]. It has also been established that some, at any rate, of the carbon atoms in the side-chain are part of a carbonyl (i.e., $-C=O$) or aldehydic (i.e., $-CHO$) group, and that methoxyl ($-OCH_3$) groups are attached to the benzene nucleus.

The chemical properties of lignin, therefore, suggest that it should have one of the characteristic properties of a resin, namely, that of polymerization. There is, in fact, considerable support for the theory that lignin, as it occurs in wood, is a complex substance, which has been built up from a number of comparatively simple units of the same nature. Further evidence in this direction is obtainable from an examination of the ultra-violet absorption spectrum of lignin; by the examination of the products obtained when lignin is hydrogenated under pressure (viz., mainly cyclohexane); and from the effects of oxidation which results, in particular, in the formation of veratric acid. Following results of this nature K. Freudenberg[5] has deduced the following structural formula for lignin:—



This formula cannot, however, be regarded as final, since it does not account for all the known chemical properties of lignin. For instance, some of the most charactertistic qualitative tests for lignin depend on its reaction as an aromatic phenol, and although the above structural diagram accounts for the presence of $-OCH_3$ groups, it does not show any true phenolic $-OH$ groups.

In practice, however, it is not usual or necessary to regard lignin as having a definite chemical identity, or even as a substance of constant chemical composition. It is more convenient to characterize it in terms of the method used to isolate it, since, as already pointed out, it will vary according to the procedure used; the more important of these methods are indicated below. Convenient as this is for many purposes, it introduces difficulties in the analytical determination of the lignin content of a material. Such a determination may be a matter of some importance, since although wood is recognized as unique in that it is the commonest and most abundant source of lignin, different woods vary considerably in this respect (see Table 1), and, indeed, the lignin may even vary in quantity from one part to another of the same tree. Thus, in general, the lignin content of sapwood is greater than that of the heartwood for the softwoods, and vice versa for the hardwoods, and it is greater for the spring wood than for the summer wood of a tree. It may also be necessary from time to time to investigate the value in this respect of other, less-known plant materials, i.e., other than wood (cf. Table 1).

Estimation of Lignin in Wood

In a method of analysis favoured by workers at the U.S. Forest Products Laboratory, following a comparison of four well-known methods,[6] the sample is converted into dry ground sawdust (40-60 mesh) from which the oils, fats, waxes and resins are removed by extraction for 48 hrs. with a mixture of 2 vols. of benzene and 1 vol. of alcohol. The residue is then digested for 3 hrs. under a reflux condenser with hot water, and then with 15 c.c. per grm. of 72 per cent. sulphuric acid at 20 degrees C. for 2 hrs.; the acid is then diluted to 3 per cent. strength, and after a further 4 hrs. of digestion at the boiling point, the residual lignin is filtered off in a tarred alundum crucible

and washed with hot water until the washings are neutral in reaction; it is then dried at 105 degrees C. and weighed, allowance being made for the ash. The result, therefore, is expressed in terms of the matter remaining insoluble under the empirical conditions of the experiment, and on this account it is open to criticism. One reason for this is because with certain woods the process of pre-extraction may not be entirely effective, and a proportion of resistant gums may be included in the insoluble matter weighed as lignin. As it stands, however, the method represents a reasonable compromise in a difficult problem; it certainly enables woods to be classified according to the proportion of their lignin content which is available for plastic manufacture; this is a justification for its inclusion at this stage, especially as the above analytical method follows, in principle, at any rate, one practical method of isolating lignin (see below).

Methods of Isolating Lignin
(a) Directly from Wood

We may, therefore, now pass on to deal with the methods of isolating lignin. As already indicated, these may be regarded as falling into two categories, according as the lignin is extracted directly from the wood or from the waste liquors rejected from one or other of the pulping processes. Methods of the former type are sometimes regarded as academic, since it is those of the latter type which are usually the basis of existing practical methods. Nevertheless, the former are worthy of brief mention, because the theory of to-day is so often the practice of to-morrow, and the fact that the methods used hitherto have so frequently been dictated by expedience or convenience (e.g., utilization of waste liquors), does not preclude the eventual development of the other possible methods. Moreover, as will be shown later, it is not necessarily essential to remove the lignin from the wood in order to utilize its plastic properties. Extraction with an organic solvent is the best example of the academic type of method, and benzyl alcohol has been used by L. Friedman and C. R. McGully.[7] The method of pretreatment described above in connection with the determination of lignin is first applied. The residue is then heated under reflux for 1 hr. with benzyl alcohol containing 3 per cent. of hydrochloric acid, and filtered while hot and washed with the hot solvent. The filtrate is then cooled and poured into a large volume of ether, with rapid stirring, and after standing for one day the lignin may be removed by filtration and washed and dried in a vacuum at 50 degrees C. A further quantity is obtained by evaporating off the ether, concentrating the residual benzyl alcohol solution in a vacuum and again pouring this concentrate into an excess of ether. The obvious disadvantage of this method from a practical point of view is the use of solvents, which would have to be recovered to make it economical; on the other hand, with solvent methods the lignin obtained is not decomposed or altered by any chemical reaction, although, of course, it may then comprise only the " native " lignin as distinct from the lignin bound as ligno-cellulose (see above).

Most of the methods in which the wood is the starting material, however, usually depend on the selective hydrolysis and consequent solubilization of the non-lignins; the analytical method described above is one instance, but hydrochloric or other mineral acids, organic acids (either added purposely or those naturally present in or developable in the wood) have also been used (by E. C. Sherrard and E. E. Harris[8]). Alkaline reagents and even fungi or enzymes natural to the wood may be used to effect the desired hydrolysis and so to liberate the lignin. Another type of process which (according to O. W. Willcox[9]) has reached the stage of full-scale operation in a pilot plant in Louisiana, goes to the other extreme in that most of the constituents of the plant except the lignin and other mouldable products are rendered soluble. Thus, according to a U.S. State Patent[10] (by

E. C. Sherrard, E. Beglinger, J. P. Hohf and E. Bateman of the Forest Products Laboratory), 100 parts of the finely ground plant material (e.g., sawdust) are autoclaved with 100 parts of water and 20 parts of aniline for 3 hrs. at 160 lb. per sq. in. (steam pressure). The resulting product (yield, 85 to 95 per cent.) may be washed, dried and powdered, and it can be moulded at 135 degrees to 190 degrees C. under a pressure of 1,500 to 3,500 lb. per sq. in. Furfuraldehyde (e.g., produced by the hydrolysis process) may be added as a plasticizer, and the working of the plastic is eased by the addition of zinc stearate as a lubricant.

Chlorination or sulphuric acid is also used in a similar way, the latter for the hydrolysis stage (in place of aniline), but the choice of reagent and cooking conditions depends on the purpose for which the final product is required. Thus the more drastic the conditions the higher the lignin content; and, in general, the lower the ratio of lignin to cellulose, the higher the strength and the poorer the resistance to water, and vice versa. I. P. Losev, V. S. Kaminski and S. V. Shiskin[11] have worked on similar lines in Russia, except that they neutralize the humic acids formed during the reaction with lime or baryta, and thereby obtain mouldings which are more resistant to water and withstand even 25 per cent. sulphuric acid. Much of the work along these lines carried out in the United States[12] has been concerned with hardwoods such as maple, oak and hickory.

(b) Utilization of Waste Pulping Liquors

We may now conveniently turn to the type of method based on the utilization of the waste liquors from the cellulose pulping process as the starting product. In such cases the lignin is, of course, rendered soluble by the alkaline or acid pulping reagent used in the pulping process and then reprecipitated. Processes of this nature are, however, limited in the case of sulphite liquor, because, as pointed out above, the lignin is rendered soluble by an alteration in its chemical properties (i.e., by the formation of lignosulphonic acid) and under these conditions it loses its plastic properties. Such processes do, however, exist. Thus G. C. Howard[13] adds lime to precipitate first the sulphites (as calcium sulphite), and then the lignosulphonic acid (as the calcium salt); the latter is separated, and treated with alkali so as to produce the flavouring matter vanillin, which may be extracted with organic solvents. If the residual liquor is then heated in an autoclave with wood chips, a plastic mass is obtained which may be pressed into sheets or dried and powdered ready for moulding. F. J. Wallace[14] prefers to treat the sulphite liquor directly with phenol and formaldehyde, thereby forming a resin of the insulating type; while, in a similar method these same reagents are used at 100 degrees C. with desulphonated lignin produced by treating the hot sulphite liquor under pressure with sodium hydroxide; fillers may be added.

Soda Process Liquors

From the industrial point of view, however, the waste liquors from the soda process are probably of more importance, and the process now operated commercially (although as yet only on a small scale) by the Mead Corporation in Ohio, U.S.A., and described by M. Plunguian,[15] is of special interest. It depends essentially on the precipitation of the lignin by the acidification of the black liquor, by means of carbon dioxide from flue-gases from a Spencer coke-burner. The gases contain 15 to 17 per cent. of carbon dioxide, and about 2 lb. of the former precipitates 1 lb. of lignin; this quantity, however, corresponds with only about 35 per cent. of the total amount of carbon dioxide actually used.

The gases are injected by means of a compressor into a closed tank holding 2,000 gallons of the liquor, the specific gravity of which is adjusted to 1.10 by evaporation; this corresponds with 11 to 12 per cent. of soluble organic solids and with about 7 per cent. of sodium carbonate. The gas which escapes passes into a second liquor tank, and this serves to absorb any unabsorbed carbon

dioxide, the proportion of which increases as the reaction in the first tank approaches completion. Precipitation in the first tank is complete in 8 to 9 hrs., and the pH value has then fallen to 8.3 to 8.5. The precipitate is fine and gelatinous, and it must therefore be coagulated by heating to 90 degrees C. and then immediately cooled to 40 degrees C., with continuous agitation. It can then be filtered in a press (capacity, 22 cubic ft.), the filtrate (which contains a certain amount of unprecipitated organic matter, see below) being evaporated and the residue burned so that the sodium compounds it contains may be converted into sodium hydroxide by causticization with lime in the usual way. The filter-cake is washed.

Properties and Uses of "Meadol"

The resulting paste, which now contains 75 to 80 per cent. of water, is dried on a double-drum drier until the moisture content is 2 to 4 per cent., and then ground to a fine powder and stored in sealed cartons. The ash content of the final product is 1.0 to 1.3 per cent., the m.pt. is 210 degrees to 235 degrees C., the methoxyl content 21.5 per cent. on an ash-free basis, and the yield is equivalent to about 30 per cent. of the total organic matter in the original liquor; it is known as "Meadol." It is insoluble in water, dilute mineral acids or non-polar organic solvents (e.g., ether and petroleum spirit), but soluble in dilute alkali solutions and most polar organic solvents.

A recent Mead Corporation patent (H. J. Reboulet[16]) introduces minor modifications into the process as described above. The black liquor should contain 16 to 17 per cent. of solids after evaporation, and the gases are passed through it at pH 7.8 to 9.0 at 20 degrees C., Turkey-red oil being used as an anti-froth. The lignin is coagulated by heating at 50 degrees to 90 degrees C. and cooling, and it is dried at a temperature below its melting point.

C. W. Scott[17] has patented a method in which the lignin is precipitated from soda liquor in a similar way, but then dissolved in ammonia and treated with formaldehyde, while Losev and his coworkers (loc. cit.[11]) condense the alkali lignin with furfuraldehyde with soda as a catalyst; the resulting product is mixed with an equal volume of wood flour in furfuraldehyde solution, and the mass can then be pressed into blocks which have great hardness.

In considering the uses to which this lignin plastic may be put, it is evident that these will be dependent on the type of lignin obtained, and, consequently, on the process of preparation used. Some of these applications have been indicated above, in so far as they involve condensation reactions. "Meadol" is essentially a moulding material, and if it is used directly as a binder in admixture with fibrous materials it may be formed into a hard dense board. On the other hand, it is an economical proposition to mix it with other plastic moulding powders, e.g., of the phenol-formaldehyde type, and up to 50 per cent. may be added in this way. The best results are, however, obtained by using "Meadol" in place of about half of the phenol or cresylic acid during the preparation of the thermosetting resin, since the resulting moulding powder is said to flow and cure well, although it is slightly inferior to a normal phenol-formaldehyde powder by reason of its slightly decreased strength and poorer water resistance.

(To be continued)

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World's Industry Employs Plastics

GENERAL ENGINEERING

Shaft packing and sealing in synthetic rubbers were recently tested by Diegmann and reported in Kunststoffe 1941/31/93 (see also "Engineers Digest," 1941, October, page 391). As compared with leather, Buna packing proved superior in almost every respect. Some care is necessary in design and arrangement when using these materials. Synthetic rubber packings should be so fixed that they cannot rotate, whilst in order to reduce friction only the end of the gland should press against the shaft. Gland length should be $\frac{3}{8}$-$\frac{5}{8}$ in., although in some improved designs this has been reduced to $\frac{1}{4}$-$\frac{5}{16}$ in. To obtain optimum results the shaft itself should be turned and ground and, if possible, polished, the greater the speed of rotation the finer the polish required. Bedding of the packing on to the shaft must be carefully attended to, as sharp edges may cause scoring or the shaft itself may damage the rubber surface. Shaft surface and rubber ring should always be kept well lubricated with suitable lubricants. Maximum speeds depend on efficacy of heat dissipation and air circulation for cooling. The life of the packing is said to equal that of standard roller bearings. **Water-pump sealing** developed by the Crane Packing Co., Chicago, Illinois, consists of bellows of synthetic rubber provided with flange ends. Contact surfaces are grooved ensuring positive seal at both the washer and driving ends. The seal is held in position by a spring which presses against the inside shoulders of the pump casing and bears against the flange end of the seal, which is symmetrical in shape and cannot be inserted in the wrong direction. **Rubber bolster mounting** for press tools described in B.P. 540,531 comprises the back plate of sheet metal, upon which is mounted a frame, say of cast-iron base. A flange extends at right angles to the back plate and faces inwardly. The flange is seated accurately on the outer edges of a resilient rubber bolster, provided with metal inserts, consisting of rectangular nuts regularly spaced. The flange has openings through which pass fixing screws and which engage the inserts. The frame is secured to the back plate by countersunk screws, whilst the flanges are stiffened by triangular rims.

AIRCRAFT

Gliders fabricated in resin-bonded plywood can assist in economy of strategic raw materials, according to Litchfield, of the Allied Aviation Corporation, writing in the February issue of "Machine Design." De Bell, plastics research engineer of the Glenn Martin Co., in the same journal, emphasizes the need for further research on resin-bonded plywood. **Specification and standards for plastics** recently formed the subject of a conference held by the Army Air Corps at Dayton, Ohio. Members of the plastics industry and representatives of interested governing departments and agencies attended. Among the points considered were problems on the tensile and compressive properties of plastics, their sheer and fatigue strength, hardness and durability and their use as bearings. An outline was drawn up to facilitate comparison and evaluation of various research developments in plastics.

ELECTRICAL

Electrical and physical properties of Lucite (acrylic resin) and Karolith (casein), were recently investigated by Rinehart, "Journal of Physics." Specific energy loss and frequencies in the neighbourhood of 50 kilocycles and Young's Modulus were measured over a temperature range of − 55 degrees to + 65 degrees C. for Lucite, and + 25 degrees C. to 110 degrees C. for Karolith. Reciprocals of Young's Modulus plotted against temperature gave positive curves at higher temperatures in both cases. At room temperature Young's Modulus for Lucite and Karolith is 4.75 by 10^{10} and 6.14 by 10^{10} dynes/sq. cm. respectively. Specific energy loss varies with variation in frequency for both materials, the variation for Lucite being linear at room temperature. In the presence of absorbed water marked anomalies occur.

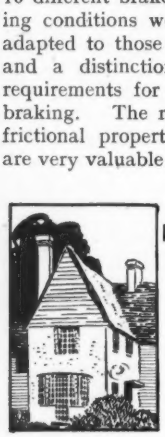
CHEMICAL

Foils between 0.02 and 1 mm. thick are now being produced in Germany by improved rolling processes. Chemically resistant plastics drawn into foils 0.3 to 1 mm. are finding extensive use in chemical apparatus. Thinner foils 0.02 to 0.04 mm. in thickness are being extensively used for electrical insulation besides special packings and wrappings. They are displacing metallic foils in many instances, and, in combination with other packing materials, such as waxed paper, are being employed where impermeability to moisture must be of the highest order. **Process for coating metals** with the polyvinyl chloride resin Igelit for conferring high corrosion resistance has been dignified by the coining of the word "Igelierung." The word "Igel" means hedgehog and would seem somewhat appropriately applied to a plastic so resistant to corrosion. P.C. synthetic fibre textiles are claimed in Germany to possess properties superior to any so far encountered among synthetic materials of this type. They are of the polyvinyl type and their resistance to acids, alkalis and a number of corrosive chemicals renders them extremely valuable in the chemical industries. In the treatment of mineral alloys, for example, with concentrated sulphuric acid, filter cloths of P.C. have a life of four-six weeks against two-three days for similar components in cotton. A 6-7 per cent. sodium hydroxide solution, which causes cotton to deteriorate very rapidly, has no effect on P.C. For the filtration of formic acid, woollen filters had a life of four-six weeks, textiles in P.C. are unaffected. The material has an extremely low water absorption and is not attacked by any bacteria. **Valves and packings of synthetic resins and rubbers** are finding increasing use in the German chemical industries and are tending to replace still further parts similarly made in metals. "VDI. Zeitschrift," 1942/86/162, presents a survey, which includes developments of this type. A valve for handling acids is constructed in the main of an asbestos-filled phenolic (Haveg). The valve is provided with a rubber sealing ring. In some instances metals otherwise unsuitable, such as low-grade cast irons, have been turned to good account for handling acids by suitable protection with rubber.

MOTORS

Brake linings consisting of a matrix of synthetic resin of different types, together with reinforcing and heat-distributing constituents, such as aluminium wool, were recently investigated by Kutsbach and Neumann. A detailed

report of this work is contained in "VDI. Zeitschrift," 1942/86/199. Fifteen different compositions, mainly embracing phenolics, with additions of aluminium wool, were examined and were tested on 10 different brake-drum materials. Testing conditions were, as far as possible, adapted to those encountered in service, and a distinction was drawn between requirements for normal and emergency braking. The report indicates that the frictional properties of these complexes are very valuable.



BUILDING

Pre-fabricated houses constructed of resin-bonded plywood and designed to mitigate the housing shortage, are described in "Machine Design," for March, 1942. It is pointed out that in this way economies are effected in the use of wood, whilst the quantities of resin used are small.

MISCELLANEOUS

Plastics production in Germany for 1940 indicates the extent to which the synthetic resins are replacing or assisting in the economizing in metals. In 1940, total plastic consumption amounted to 60,000 tons, estimated to result in the saving of about 300,000 tons of iron, steel and non-ferrous metals. Between 1936 and 1940 production of plastics of the phenolic and cresole types increased by 125 per cent. Phenol and cresole output for the same period was increased by 150 per cent. It is stated that recovery of phenol and cresole from coke-oven and gas by-products has reached an efficiency of 100 per cent. Between 1935 and 1940 output of thermo-softening resins increased tenfold. **Classed in Japan as artificial fibre No. 1,** a new synthetic developed in Kyoto University is said to surpass in mechanical and other properties those of nylon, vinnon and P.C. Breakage strength is said to be four times that of natural wool fibre. Production costs are claimed to be lower than those of any other fibre. Plant hitherto manufacturing viscose is said to be readily adapted for producing the new material. **Cellulose wool production** to the extent of 20 tons per day is projected for a new factory being erected near Borregaard in Norway. Norwegian and German interests are concerned. Rice straw cellulose to the extent of 3,000 tons per annum and by-product fibre to the extent of 7,000 tons per annum are to be produced by a company recently formed in Valencia, operating under Japanese licences; 47,000 tons of rice straw per annum will be required. The produce is intended to take the place of cotton and natural silk. **Cost factors of design for plastics,** more especially when the latter are replacing metals, are discussed by Delmonte in "Machine Design" for March, 1942. It is pointed out that prime cost on a sound basis may make plastics appear expensive as compared with metals, but when total production costs are analysed advantages lie with plastics in speed of production and decrease in number of finishing and handling operations. On a basis of cost per cubic inch, phenolics are the cheapest and acrylics the most expensive plastics. Moulding costs may generally be considered as composed of fixed initial costs, plus a factor proportional to the number of cavities. In place of expensive steel moulds, Delmonte has developed a zinc alloy mould for experimental and small quantity production. Ultimate cost per item of finished work is shown to depend largely on the number of parts produced. In one particular example analysed cost per workpiece for outputs of 100, 1,000 and 25,000 were 13 cents, 9 cents and 7 cents respectively; material cost being assumed at 5 per cent. of total cost. Production by machining is considered.

Plastic Building Components

The author continues his notes in the May issue with the design groups comprising small plastic moulded units and transparent building components. As before, he deals in each section with existing practice and with possibilities in plastics, but it must be realized that these suggestions are in the nature of guides for both architect and plastic manufacturer, rather than of concrete examples

By G. FEJÉR

SMALL FITMENTS

Plastics have already made many friends on the strength of the quality of small fitments, electric appliances, etc., which are in wide circulation. One is inclined to think that small objects which are required in large quantities are especially favoured by the plastics trade. This is probably true because of the structure of the industry as a mass-producing one on the whole and because of the nature of the manufacturing plant. So far as the building trade is concerned, there is plenty of opportunity for using a good deal more useful little gadgets and appliances made of plastics.

Established Forms

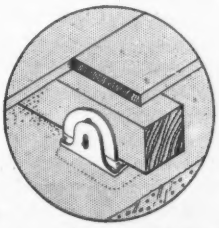
Colour and "showiness" of fitments is not always required. Naturally there is a large business in pleasing fitments which appeal to everybody, especially to the handyman and householder; but it may be well worth going into the matter of the supply of those fitments which are present in many constructions, doing their duty modestly. Instead of describing many of the established shapes of this kind, the writer gives a few suggestions on small units which could be carried out by using plastics. Hinges, knobs, handles and all kinds of items of ironmongery will make further progress; the examples given below entail the study of new problems, although their use seems quite possible.

The question of such sundry materials or accessories is quite important as there is a steady market for them, and the manufacturer is not affected by sudden changes in shapes or colours. The only thing that matters is whether the component does the job more efficiently at a reasonable cost.

Concrete construction, masonry, carpentry and all other branches of the building trade use a number of such small units.

Let us take as examples two of the possibilities: floor clips (floor springs) and wall ties.

Floor Clips.—When reinforced concrete floors are covered with wooden flooring, floor clips are employed to secure the battens (say 2 ins. to 3 ins. wide) to the concrete. Generally three or four clips per sq. yard are being used. The sketch



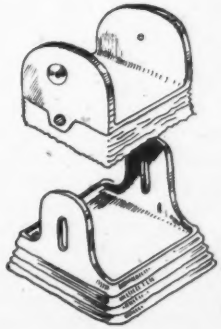
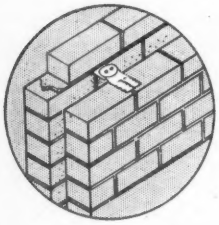


Fig. 6.—Floor clips of plastics.

shows the shape which the writer suggests for production in plastic material. A felt cushion is used to reduce transmission of shocks and sound.

Wall Ties.—Double walls with a hollow space need wall ties for various reasons, but it should be noted that the wall ties must not form bridges of heat conduction, thus reducing the insulation value of the double wall. Purpose-made bricks, galvanized iron, wrought iron, or sometimes steel-cored copper elements can be used for the purpose (they are employed on every 3-ft. horizontal and in 18-in. vertical distances). The suggestion for a plastic wall tie consists of two elements bolted together; an additional layer of insulating material may be included.



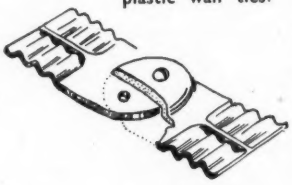


Fig. 7.—Suggested plastic wall ties.

TRANSLUCENT COMPONENTS

Established Shapes

So far as the building trade is concerned translucent structures are invariably made of glass—a material which is so well known to readers that any further enumeration of the various types is hardly necessary. Glass is a highly durable and excellent building material with outstanding qualities as regards ageing, etc.

Let us however concentrate on a few questions less frequently discussed in order to locate those points where the suitability of plastics can be anticipated.

When we speak of "ordinary glass" we generally think of one type or another of the plane-parallel glass sheets of traditional kind which are (according to their manufacture) also known as flat drawn sheet glass, blown glass, polished plate glass, rolled glass, pressed glass, etc.

The sizes, thicknesses, surface treatment and general appearance may differ—nevertheless the main characteristics of these various kinds of building-glasses are very much the same.

The highly specialized types of window- and roof-glazing sheets have been developed through centuries of improvements in the manufacture and application. The glass industries have made it easy to allocate transparent structures for every possible type of building work.

But it is not only the glass which has adapted itself to building requirements — the correlation between architecture and the industry is a much deeper one—the characteristics of glass have markedly influenced the whole story of the architectural means of expression.

When we speak of a façade, we generally think of a wall surface punctured with "holes" into which the glazing is fixed.

The necessity of framing sheet-glass leads to frame-structures (windows) of totally different character to the non-transparent wall structures. We still work under this tradition.

Let us compare for argument's sake two sections of a wall—the translucent section with a non-translucent section—and examine what are the inherent differences of the two. Supposing the window section A—A is compared with the adjoining light wall structure B—B built of rigid sheets, for a semi-temporary building (see Fig. 8). The following considerations may be noted:—

(a) Erection and Labour. The wall can be either pre-fabricated in large sections or made in situ by using simple methods of construction. The window requires fitting, glazing, painting

" in situ," and considering all the operations involved it requires a much higher rate of labour/p. surface than the wall.

(b) Heat Losses. The performance of the wall unit may vary between 0.18 and 0.3 B.Th.U. per sq. ft., hour, degree F. The window glass itself has a transmittance value between 0.7 and 1.02. This great difference in transmittance values works out in considerable quantities of fuel " lost " in every heating period (provided that modern methods of heating are being applied). Apart from this the air infiltration around the glass might be anything between 72 and 268 cubic ft./hour/sq. ft. (according to Kent); on the wall unit, however, no such amount of air infiltration is likely to occur.

(c) Acoustic Considerations. The wall unit as a hollow structure will show a more favourable capacity for reducing the transmission of sound than the single sheet of glass.

The reflection of sound is another important consideration for certain types of interiors. It is often desired that the wall as a surface should absorb rather than reflect the oncoming waves of sound. The polished surface of the glass sheets may absorb 2-3 per cent., whereas the wallboards made for such purposes show absorption coefficients ranging from 25 per cent. to 70 per cent. on the average (taking the " open window " unit as 100 per cent.).

These considerations show some of the inherent disadvantages of the vertical glazing, but this is only one side of the picture, and nobody would deny the advantages as well as the absolute necessity of glazings. The window as illustrated in the sketch is not only a source of draught, heat losses, noise—but is also a source of daylight, view, sun heat and ventilation.*

Of these, daylight is the most important factor, as " view " may not always be essential. " Sun heat "—or better—infra red radiation contained in daylight, develops a considerable quantity of heat behind the glazings. As a general rule, it is inevitable that materials such as glass transmitting the visible rays of the sunshine automatically transmit the infra-red rays, too. The " free supply " of heat thus gained is very welcome during a heating period of, say, 200 days per year. (It can also prove a nuisance in summer and in hot climates.)

In thermostically controlled, air-conditioned buildings such " free supply " of heat provides a considerable reduction of fuel consumed. The sun heat gained, however, is not nearly enough to balance the high heating losses occurring in the usual types of windows.

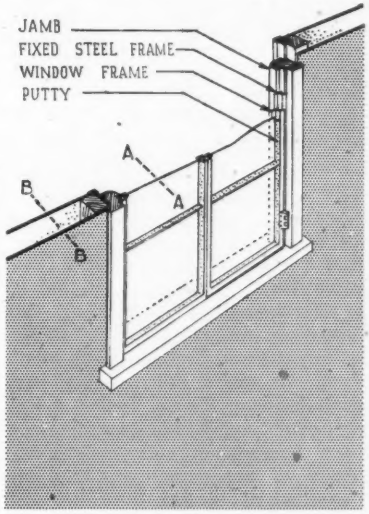


Fig. 8.—Sketch of window and method of fixing.

The above comparisons may be summarized therefore in the aims for certain improvements on the translucent structure. These aims are:—

(1) To improve upon the insulating properties of the translucent structure;

(2) To provide translucent structures more or less in the same manner of erection as the wall surface itself, with simi-

* The writer does not think that translucent structures must of necessity be considered as a source of ventilation (except in domestic buildings). Whenever possible the exchange of air should be based on automatic air conditioning rather than opening windows.

lar manners of fixing, similar textures of the surfaces, etc.

These two aims have so far led to a number of more recent types of glass products, such as **glass blocks, lenses** (for pavement lights, roofs, etc.) usually in conjunction with reinforced concrete. Certain glass-concrete sections are often precast in specialized workshops. **Hollow glass blocks** often made in two parts and used either in conjunction with reinforced concrete or in a similar manner to ordinary bricks to erect strong and fairly well insulated glass walls. **Three-ply glasses** have been developed for the purpose of improving the insulating properties of sheet glass, and are built up from two glass sheets with a layer or layers of glass-silk in between.

Suggestions for Plastics

The above notes on glass may already give a lead as to the lines on which future developments can be expected. The aims, which lead to improvements on glass, and to the creation of modern types of glass building components, can be also achieved by using transparent plastics.

(The writer has already dealt with some aspects of the possibilities of translucent plastics in previous articles on these pages ("Isolumen," October, 1940; "Building with Plastics During the War and After," September, 1941) and some of the suggestions contained in those notes have been introduced to the building market.)

So far none of the transparent plastics can compete with glass so far as window-glazings of domestic buildings are concerned. It cannot be emphasized too strongly that the future of organic glazings is the most promising for those uses only where the application of glass is not desirable.

Therefore the writer would suggest two groups of components for closer investigation:

(a) Translucent, semi-rigid boards.

(b) Translucent hollow slabs or blocks.

Both groups include large possibilities for developing suitable designs.

Let us attempt to provide translucent structures which in their function as well as method of erection are equivalent to their adjoining wall structures. This means that instead of having walls and windows we think in terms of an insulating, protective "shell," certain portions of which should transmit daylight.

(a) Semi-rigid boards should preferably be of similar sizes and performance as the non-translucent boards. The manner of fixing could also be very similar, and the whole double wall may be regarded as a compact unit assembled by the usual method of panelling.

The sections suitable for such translucent boards may be built up by lamination (in a manner similar to that described in the April issue on these pages) by using perforated and plain sheets in several layers.

Other kinds of insulating sections have been mentioned in the September, 1941, issue. Fig. 9 shows a double wall of a light structure, and indicates the simple principle of assembling fairly large wall units for various utilitarian buildings. The supporting framework, of course, is not confined to wood, the other usual systems

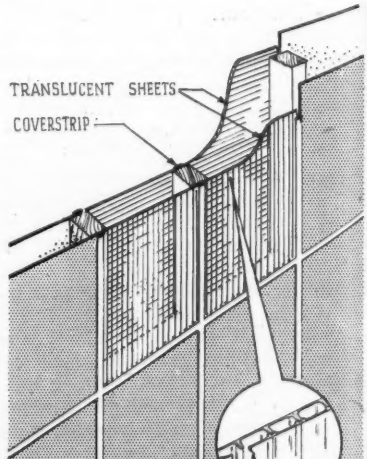


Fig. 9.—Suggestion for transparent organic glass incorporated in wall.

of supporting the boards—such as, for instance, steel bars with " wedge " or " clip " methods, asbestos cement tubes, etc.—may also be suitable.

It may be well worth considering the function of such translucent surfaces in relation to artificial lighting. Certainly it may be the logical way of providing light (both daylight and artificial) through the same surfaces. Details of this problem, however, would certainly lead us too far from the subject.

(b) Translucent Hollow Slabs.—Under the heading " Finished Articles " the writer described a suggestion for hollow slabs (Fig. 5). If we provide translucent slabs of similar shape, certain parts of a partition wall (or external wall) can provide daylight without changing the uniformity of the assembly method by windows, glazing-bars or the like. The principle is the assembling of complete wall sections in workshops, including " glazing." The slabs themselves need not be large, as smaller sizes may prove more versatile as well as easier to manufacture.

The Present Practice

When dealing with the problems of translucent building components it may be as well to comment on the various plastic materials (mostly cellulose acetates) which have been developed solely for building uses to meet the requirements of war-time building. The " Glass Protection Order " (Ministry of Labour) and various recommendations and other instructions of the authorities have made it necessary to investigate the problems of " splinterproofing " and " substituting " glass.

It is too early yet to sum up the technical achievements, successes and warnings on uses, fixing, etc., of the various products, although the position is much clearer now after the guidance of the authorities concerned.

The revised Bulletin C.10 has been issued by the Min. of H.S. Research and Experimental Dept. The Building Research Station (Watford) as well as the N.P.L. have carried out extensive tests, and various considerations (in consultations with the M.O.W.B.) have played a part in reducing the number of the approved products.

From the 550 various products and methods tested there are only a few which have been approved, and so far as organic glazing materials are concerned, eight products have been described as " sufficiently stiff for fixing by the usual glazing methods."

As some of these products had certain peace-time uses and others may be the forerunners of " semi-rigid boards " of a more substantial type, it may be of interest to quote some of the details described in the Bulletin C.10. The eight products mentioned are the following:—

Trade Name	Type	Sizes	Per cent. of daylight transmitted*
Armourbex ..	Wire reinforced	55" × 24"	59
British Celanese F.42/4 ..	Wire reinforced	36" wide	65
Celanet F.12/12	Textile reinforced	36" wide	37
Celanet F.12/8	Textile reinforced		40
Isolumen ..	Homogeneous	20" wide	74
Sunralite ..	Wire reinforced	36" wide	59
Windolite ..	Wire reinforced	36" wide	63
Wirelite ..	Wire reinforced	3', 4', 5' and 6' × 2'	48

* Approx. 85% for clear transparent glass.

It will be seen that most of the products are reinforced with wire netting, some with textile, and one without such reinforcement.

Conclusion

In the previous notes the writer has attempted to deal with the aspects of plastic-building components from the point of view of design and the performance expected. No particular plastic has been mentioned for any of the suggested shapes, as the multitude of the substances available makes many alternatives possible.

The whole field of the " designed " plastic building components has been divided into seven " design groups," according to their shape, omitting the very important field of application of

POSSIBLE APPLICATIONS OF PLAST

TYPE OF BUILDING WORK	PLIABLE SHEETING	RIGID SHEETING	TILES	LATHS, EXTR
AIR CONDITIONING		Air-ducts	Perforated tiles	Louvres, air in coverstrips
CARPENTRY	Veneers, linings	Doors, laminations, wall-lining		Handrails, c beadings, gu
CONCRETING		Shuttering, Lining	Lining of walls, ceilings, etc.	Fixing rails (en
DECORATING	Curtains, wall, ceiling, etc., linings, screens	Wall-lining	Lining of walls, ceilings, etc.	Handrails, cu pelmets, ski
ELECTRICAL	Insulating sheets	Switchboards, etc.		Tubes, cabl channels
FLOORING		Floorboards	Floor tiles	Skirtings, str flooring (Te
FOUNDATIONS	Inter-layers	Shuttering, expansion joints		
GLAZING		Obscuration shutters		Glazing bars, tions, beads windows
HEATING			Fireplace parts	Louvres for ai
IRONMONGERY		Protective plates (on doors, etc.)		Guide rails, fi
LIGHTING		Structures for indirect light		Coverstrips, elements
ROOFING	Roofing sheets	Roofing boards	Roofing tiles	Laths
SANITATION	Shower-curtains	Bathroom lining	Bathroom, kitchen, etc., lining	Pipes, hollow
SOUNDPROOFING	Quilt-type sheets	Internal linings	Acoustic tiles	Elements for pended ceil
INSULATION	Quilt-type sheets	Insulating boards	Internal linings	Draught coverstrips

F PLASTICS IN BUILDING

LATHS, EXTRUSIONS	FINISHED UNITS	SMALL FITMENTS	TRANSPARENT UNITS
Louvres, air inlets, angles, coverstrips	Fans, filter parts, air-changer units	Control instruments	Air inlets
Handrails, coverstrips, beadings, guide rails	Built-in cabinets, drawers, frames	Ornamental fitments, knobs, etc.	Partitioning, sliding and folding doors
Fixing rails (embedded)	Hollow blocks	Fixing devices	"Glazed" precast units
Handrails, curtain rods, pelmets, skirtings, etc.	Picture frames, decorative fitments	Ornamental fitments	Laylights
Tubes, cable covers, channels	Instrument bodies	Switches, etc.	Dials and controls
Skirtings, strips in cast flooring (Terrazzo)	Hollow blocks (in concrete)	Floorclips	
		Fixing devices	
Glazing bars, frame sections, beads for metal windows	Window frames, cloche frames, greenhouse sections	Glazing sprigs	Hollow blocks, rigid sheets, horticultural sheets
Louvres for air heaters	Radiator bodies, fireplace surrounds	Controls, switches	
Guide rails, fixing rails		Hinges, handles, knobs, etc., brackets, angles	
Coverstrips, framing elements	Lamps, shades, reflectors, etc.	Switches, sockets, etc.	Shades, screens
Laths	Ventilators, eaves	Fixing devices	Translucent roofing sheets
Pipes, hollow sections	Built-in equipment, baths, washbasins, lavatory seats	Taps, siphon parts, showers	Sliding doors for built-in cabinets
Elements for fixing suspended ceilings, etc.	Hollow blocks	Insulated fixing devices	Cellular sheets
Draught excluders, coverstrips, etc.	Hollow blocks, refrigerator equipment	Fixing and distancing devices	Cellular sheets, hollow blocks

plastics such as paints, finishes, adhesive compounds, etc.

Taking the various described design groups on the one hand and some of the important types of building work on the other hand, the possible future applications of plastics could be tabulated in a systematic manner. The writer gives a short version of such a table on pages 180 and 181. Although only a few of the numerous types of building operations are mentioned, the table shows that there are possibilities for every building specialist (or contractor) of using plastics of different types. On the other hand, the vertical columns indicate that the same kind of plastic component may be used by building specialists whose scope and status is very different. As some of these contractors are potential clients, it can be seen that marketing and distributing problems of plastic components may not be quite simple.

It seems, therefore, obvious that the future of plastic building components is by no means confined to certain groups of products, such as, say, extrusion mouldings or rigid sheetings. To prepare the components, to investigate all the preliminary questions is in the interest of nearly every plastics manufacturer, moulder or fabricator. The number of problems involved is formidable, and it is unlikely that the smaller firms can succeed in popularizing plastics for building use without some sort of concentrated support of the whole industry.

The Analysis of the Designs

The planning work, to prepare the future of building components, should begin with the collection of all the suggested designs of components, ideas, as well as previous experiments and experience on the plastic building line.

All tentative "designs" should be analysed from the point of view of:

(a) Production.
(b) Market, distribution.
(c) Use, technical aspects.

Although generally every manufacturer investigates such points minutely before going into the production of a certain article, it is suggested that an analysis should be made on new ideas and designs irrespective of whether they are going into production or not, and to have all preliminary considerations completed in advance.

(a) Production.—Scarcely any design can be strictly confined to one certain plastic as raw material, although the performance of, say, a thermoplastic lath is different from a thermosetting one. The confines of use should be tabulated and determined as to what type or kind of building work the product will be limited.

Rate of Output.—Method of manufacture is also a vital consideration, as the building trade requires components in larger tonnage than most of the industries now utilizing plastics.

(b) Market Analysis and Distribution.—Few plastics fabricators, moulders or manufacturers have facilities for dealing with builders' and architects' specifications. In future either separate departments of existing firms will have to be formed or some other sort of specialization will have to take place. The manufacturer of the chemical supplies can obviously not cope with a multitude of small orders and architectural matters.

In many cases the raw material will probably go through a chain of firms until the finished product is fixed on the job.

The availability, specifications of sizes and all matter relating to general usage of similar non-plastic components have to be studied and, when possible, improved upon.

Costs of fixing, transport, handling, insurance, etc., are nearly as important for every component as the initial manufacturing and fabricating costs. Some plastic components may be easier transported and fixed, and thus give a reasonable figure as to the final costs, although apparently too expensive when cost/sq. ft. figures are only considered.

(c) Technical Recommendations.—The designs should also be analysed most carefully from the point of view of the performance, service and maintenance, in comparison with the generally used components.

Polyvinyl Acetate Adhesives

Synthetic adhesives have already replaced many natural glues and cements because of their improved adhesive power, resistance to fungus and moisture and therefore longer life. Among the synthetic types the vinyl adhesives occupy an important place and their value is herein discussed

By
E. E. HALLS

THE adhesives comprising the resinous polymers of vinyl acetate in organic solvent solution have been known for many years. A range of them has been successfully exploited in Canada and America under the trade designations of Alvars and Gelvars, with strength and tenacity as outstanding features, and their utility has been established in a wide variety of work. Considering the almost universal need for cements and adhesives of one type or another in nearly every branch of industry, it is, at first sight, rather surprising that very little has been seen of these adhesives or of their applications in this country. The probable explanation, of course, lies in the raw materials for their production, and, fundamentally, this leads back to carbide, conspicuous by its absence from our chemical industry; this subject has already been given much publicity and is one that will rankle for ever with chemists and chemical engineers alike. Without apologies for further chafing of unhealed sores, attention is drawn to a limited range of test results on two new American adhesives of this group. They are particularly attractive as air-drying plastic adhesives, and of the type that would appeal to the investigating technician, without prior knowledge of their capabilities, as worthy of examination as multi-purposes materials for general engineering. Consequently, they have been examined as stickants for similar and dissimilar materials, rough and smooth.

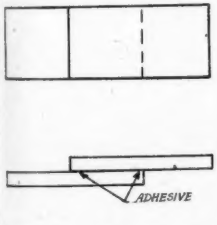


Fig. 1.—The diagrams show the arrangement of the test-piece.

Method of Test

The tests were carried out in very simple fashion. The two pieces of material to be secured were fixed by means of the adhesive in lap-fashion, as shown by the sketch, Fig. 1. The materials explored embraced the following combinations:—

(1) Phenolic resin bonded laminates to paper.

The plastic sheet represented a high grade of synthetic resin bonded paper board, with the usual hard surface in the polished condition as it leaves the press. Actually, it was a material made to B.S.S.547, grade 1, of very low water absorption, thus representing probably the worst conditions in the phenolic range of mouldings, sheet, rod or tube, for which a cement or adhesive has to cater. The thickness of the material used was $\frac{1}{16}$ in. The paper employed represented grades commonly used for labels, posters, schematics, etc., and was 0.005 in. in thickness.

(2) Phenolic-laminated to phenolic-laminated.

The same grade of sheet was used as employed in (1).

Table 1.—Lap Joints in Various Materials Using Air-drying Phenolic Resin Cement and Air-drying Polyvinyl Acetate Adhesives.

Combination No.	Materials Lapped	Air-drying Phenolic Resin Rubber Cement, No. 1	Air-drying Polyvinyl Acetate Cement, No. 2	Air-drying Polyvinyl Acetate Cement, No. 3
1	Phenolic laminated paper ..	Good	Good	Poor
2	Phenolic laminated phenolic laminated	Rather poor	Good	Very poor
3	Plywood plywood	Very good	Excellent	Poor
4	Phenolic laminated plywood	Good	Fairly good	Very poor
5	Phenolic laminated brass ..	Rather poor	Poor. Brass corroded to green copper compounds	Very poor
6	Brass plywood	Poor	Poor	Poor
7	Soft rubber plywood ..	Poor	Poor	Poor
8	Bituminized cement asbestos board bituminized cement asbestos board	Very poor	Very poor	Very poor

(3) Plywood to plywood.

The material used for the tests was actually four-ply, approximately $\frac{1}{4}$ in. in thickness.

(4) Phenolic-laminated to plywood.

This combination used bakelite sheet as in (1) and plywood as in (3).

(5) Phenolic-laminated to brass.

The laminated sheet was as in (1), while the brass was a 60/40 white brass cold rolled strip, $\frac{1}{16}$ in. thickness, hard temper. The smooth rolled surface was not disturbed by pickling or roughening in any way.

(6) Brass to plywood.

The materials jointed were brass as in (5) and plywood as in (3).

(7) Soft rubber to plywood.

The rubber employed was a common quality of good grade grey vulcanized sheet, Shore hardness value between 50 and 60 numerals, and the plywood as in (3).

(8) Bituminized cement asbestos board to bituminized cement asbestos board.

This material represented the plastics industry's substitute for slate panels, a pressure-produced cement-bonded asbestos board having a bitumen compound impregnant for improving moisture resistance and electrical characteristics. The specimens used were $\frac{1}{4}$ in. in thickness, and corresponded to the material known in the electrical industry as " self-extinguishing " grade of cement-bonded board.

The test specimens were cemented by applying adhesive to the two mating surfaces and pressing together; where necessitated by the rigidity of the materials, the joined specimens were held under light pressure overnight. They were then allowed three to four days to " mature " and fully dry out at laboratory temperatures before examination. The potential possibilities of the joints were tested by hand in a comparative manner for resistance to tearing apart.

For comparison with the two vinyl acetate adhesives, an air-drying phenolic-resin-rubber cement was used.

The results of this test are tabulated in a self-explanatory manner in Table 1. From this it will be seen that the polyvinyl acetate cement No. 3 proved unattractive, but No. 2 looked very promising and generally to have advantages over the air-drying cement. Consequently, the more satisfactory combinations, Nos. 1 to 4 inclusive, were re-explored, using the phenolic-resin cement and polyvinyl acetate adhesive No. 2. Test specimens were prepared in duplicate. One set was subjected to a mild artificial ageing test, comprising a

cycle of cool and warm, dry and wet conditions. It used a zinc-lined teak cabinet, in the base of which was placed a tray of water. The cabinet was heated by electrical heaters controlled by variable resistances. The specimens, suspended from glass rods, were exposed in the upper half of the chamber.

The test temperature was controlled at 55-60 degrees C. during the day period of eight hours, the cabinet being allowed to cool off to atmospheric temperature during the night. Humidity was maintained at 70-75 per cent. during the day and rose to 100 per cent. with condensation upon the specimens during the night.

It will be noted that the ageing test was not unduly arduous, and that the conditions are only those likely to be encountered in normal service with fluctuating day to night temperatures, except being compressed into a short period.

The second set of test specimens were kept freely exposed to air at laboratory temperatures. After 28 days, both sets were examined and compared. Results are given in detail in Table 2.

Discussion of Results

The specimens kept for 28 days all showed some improvement over those examined within three days of cementing and recorded in Table 1; this would be due to completion of drying out. With the bakelite cement, deterioration of some specimens occurred under the heat and humidity test. Thus the relatively non-absorbent combination of phenolic laminated/phenolic laminated failed, and likewise the non-absorbent phenolic laminated to absorbent wood failed. Wood to wood showed some deterioration, and only the paper to phenolic laminated stood up to the conditions really well. On the other hand, with the vinyl acetate cement, all samples withstood the conditions without deterioration.

Table 2.—Comparison of Lap Joints in Various Materials using Air-drying Phenolic Resin Cement and Air-drying Polyvinyl Acetate Adhesives, Before and After Artificial Ageing for 28 Days.

Combination No.	Materials lapped	Air-drying Phenolic Resin-Rubber Cement No. 1		Air-drying Polyvinyl Acetate Cement No. 2	
		Lab. temperature for 28 days	Hot and cold humidity for 28 days	Lab. temperature for 28 days	Hot and cold humidity for 28 days
1	Phenolic laminated/paper	Excellent. Paper could not be separated from the phenolic laminated material except by scraping	Excellent. Paper could not be separated from the plastic sheet; no deterioration under heat and humidity	Excellent. Paper could not be separated except by scraping	Excellent. Paper could not be separated from the plastic sheet; no deterioration due to heat and humidity
2	Phenolic laminated/phenolic laminated	Very good, the two pieces of sheet separable only with difficulty	Poor, deteriorated by heat and humidity, the two pieces of sheet being easily separable	Excellent, the two pieces of sheet being inseparable	Excellent, no deterioration due to heat and humidity
3	Plywood/plywood	Very good, the two pieces of wood separable only with difficulty	Good, but a little deterioration due to heat and humidity, and the junction could be separated a little more easily	Excellent. Wood torn without break at cemented junction	Excellent. No deterioration due to heat and humidity. Wood torn without rupture at junction.
4	Phenolic laminated/plywood	Very good, the two materials separable only with difficulty	Poor, marked deterioration due to heat and humidity, materials easily separated	Very good, the two materials being separable only with difficulty	Excellent, improved by test conditions of heat and humidity, junction separable only with tearing of the wood

Table 3.—Laboratory Characteristics of Air-drying Phenolic Resin-Rubber Cement and Polyvinyl Acetate Adhesives.

	Phenolic Resin-Rubber Cement No. 1	Polyvinyl Acetate Cement No. 2	Polyvinyl Acetate Cement No. 3
Compositional:			
Volatile Spirit (loss in weight, 3 hours at 110°C.) % ..	85.0	70.5	77.5
Total Solids % ..	15.0	29.5	22.5
	100.0	100.0	100.0
Acid Value, expressed in terms of mgms. KOH per gr. of resinous base ..	8.5	15.5	1.3

Properties of the Test Adhesives

Table 3 gives some characteristics of the adhesives employed for these tests. The phenolic-resin-rubber cement No. 1 is a widely employed type of material where an air-drying synthetic adhesive is required. It is used for securing labels and instruction charts to various materials, those of phenolic-resin base, sindanyo, metal, etc. It is also used for fixing light components in frames, glass windows, diaphragms and the like. In composition, it is an oil soluble phenol-formaldehyde resin and rubber in volatile solvents. Of the polyvinyl acetate cements, it will be noted that the more acid one, of higher consistency, proved the more satisfactory. It is this acidity, presumably due to free acetic acid, that caused corrosion of the brass test pieces as recorded in Table 1. There are, of course, applications where this would be of consequence and render this adhesive unacceptable. On the other hand, there are many instances where it would be of no consequence. In electrical applications the possibility of lowering of insulation resistance would have to be considered.

The Industrial Importance of Adhesives

To-day, with rapidity of production paramount, cementing is an essential process in engineering. Plastic components that would normally be moulded often have to be fashioned from sheet, rod or tube, perhaps in several pieces secured solidly together with adhesive. Such a condition may be a permanent one when quantities involved are small, or a temporary phase pending production of tools by an overloaded toolroom. Availability of a wide range of cements is an essential to meet the emergency circumstances. Fig. 2 shows a component fabricated in two pieces from phenolic laminated paper tube and phenolic laminated fabric sheet, securely fixed by cementing. Normally, a phenol-formaldehyde liquid resin cement, mixed 50/50 with plaster of Paris, would be employed for this type of junction, and would require baking for 12 to 18 hours at 60 to 70 degrees C., followed by 6 to 12 hours at 100 to 110 degrees C. The more satisfactory vinyl acetate cement referred to above could be more neatly applied and would give a satisfactory result without stoving.

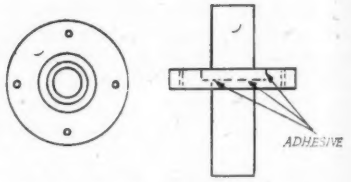


Fig. 2.—Component made from two fabricated pieces cemented together.

It is believed that at least one manufacturer is concentrating upon the production of vinyl acetate compounds, film and sheet material, and solutions for various purposes, in this country, and, therefore, the above preliminary information upon polyvinyl base adhesives should prove of interest.

Sir Cecil Weir's New Appointment

At the request of the Minister of Supply, Sir Cecil Weir, K.B.E., M.C., D.L., has been released by the President of the Board of Trade in order to take up the appointment of Director-General of Equipment and Stores in the Ministry of Supply in succession to the late Sir William T. Wilson. Sir Cecil Weir, who was Controller-General of Factory and Storage Premises at the Board of Trade, will retain his membership of the Industrial and Export Council.

INQUIRIES AND ANSWERS

(In Which is Included General Correspondence)

IMPORTANT NOTICE: If inquirers wish to receive replies by post, a stamped and addressed envelope must be included in their letter. Unless otherwise stipulated, it is understood that the submission of a problem to the Editor permits its publication in this journal.

Plastic Sheet as Instrument Covers

I have read with great interest the article by your contributor, E. E. Hall, on the use of plastic sheet for the windows of measuring instruments, and although his article was very informative, he has dealt only with the mechanical conceptions of the problem, and has completely ignored a vital point from the instrument maker's view, namely the ease with which these materials pick up a surface electrostatic charge when gently rubbed or polished. This charge develops, of course, during machining operations, and no doubt many of your readers have noticed the way in which the shavings tend to stick together and to the work. However, from the instrument maker's point of view the charges which are built up on the surface by simply rubbing the finger across it, render the material useless. The charge which may be built up in this way on a disc 2 ins. diameter is sufficient to produce a torque of 3 milligram-cms. on a pointer 1 in. long pivoted at the edge of the disc, and at a distance $\frac{1}{8}$ in. from the disc. The magnitude of the charge, which varies with the relative temperature and humidity, being worse at temperatures below freezing point, is quite sufficient to cause an error of 20 per cent. on the indication of sensitive electrical measuring instruments, and this in itself is sufficient to render the material useless for electrical measuring instruments, particularly so when these instruments are to be used in aircraft where the ambient temperature is generally below freezing point.

These facts have emerged as a result of considerable tests with "Perspex" obtained from I.C.I. and also with Rhodoid, both of which we have had to reject as unsuitable and return to the use of laminated safety glass of the normal type.

It would seem, therefore, that there is a wide need for a transparent plastic in which this property of the electro-static charge is absent. In general use this material would be considerably better than the present materials, since even when used as windows in look-outs and ports, the polishing must inevitably result in a considerable charge, causing it to act in the same manner as an electro-static precipitator and acquire a layer of dust particles, thus partially obscuring the visibility.

N. L. ADAMS,
SIFRAM ELECTRICAL INSTRUMENT CO., LTD.
Devon.

[EDITOR'S NOTE.—We believe this unfortunate characteristic is quite well known to most workers in plastic sheet and the better the electrical properties the worse it is. But doubtless, too, most attempts to remove static electricity will result in some diminution of the very advantages required in the first place. There is one suggestion we should like to make, one that is somewhat similar to the problem that faces the dry-cleaning industry where static electricity is built up in white spirit during transport in pipes or during actual cleaning operations and may result in fires. We suggest the inclusion in the resin of certain metallic organic compounds which are somewhat resinous in nature and which are transparent. They are quite miscible or soluble in most resins.]

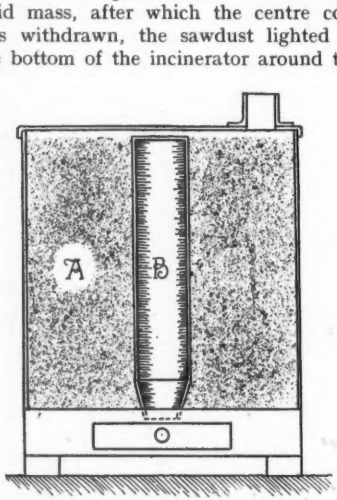
Use of Sawdust

I have read with interest in your May issue the "Sad Story of Sawdust," and think I am able to give a suggestion for the disposal of sawdust by burning it and making use of the heat thus generated.

Some years ago I saw in operation a very good burner on the Continent, which burned sawdust, the heat being utilized

for warming a room in a factory. This incinerator was cylindrical in shape and composed of sheet metal with a removable metal core.

While the centre core was in position, the sawdust was filled into the outer chamber and pressed down to a fairly solid mass, after which the centre core was withdrawn, the sawdust lighted at the bottom of the incinerator around the



Diagrammatic section of sawdust incinerator. A, sawdust; B, removable core.

opening made by the withdrawal of the core. It was found that the sawdust would burn slowly and completely, giving off a considerable heat which was made use of as mentioned above.

Enclosed herewith is a rough sketch, showing the arrangement of such an incinerator which I thought, perhaps, might be of interest to you.

TYNE TRUCK AND TROLLEY CO., LTD.
Newcastle.

[EDITOR'S NOTE.—This simple incinerator-heater is rather typical of others we have seen on the Continent. In one type, the central core was a permanent fixture made as a fire-brick cylinder provided with holes presumably to allow access of air for combustion. The cylinder also prevented the falling in of sawdust. When we examined the apparatus we thought there would be excessive corrosion from acidic exit gases in the sheet-metal chimney and hot gas ducts. Combustion was first started by a small gas jet which was then extinguished. The size of the apparatus was about the same size as the type illustrated; it had a capacity of about 50 lb. sawdust, depending on the mesh, which burned for more than six hours without replenishing.]

I read your article entitled " The Sad Story of Sawdust " with great interest, but it occurred to me that you may not know that there is an even sadder story and that is the disposal of " sander dust " from woodworking factories.

In so far as sawdust is concerned many factories have heating plant designed for utilizing their wood waste, and the mixed variety of sawdust that you refer to is used as a fuel for helping to supply heat for the factory, drying kilns, etc.

In the case of " sander dust," however, the question of disposal is a difficult one; it has explosive tendencies when discharged into a furnace or boiler which is above a certain temperature, and cannot, therefore, be mixed with the normal wood waste extraction. If some genius in the plastic industry could devise means for utilizing this by-product it would rid the woodworking industry of a considerable nuisance.

W. S. BLEWETT,
EDUCATIONAL SUPPLY ASSOCIATION, LTD.
Herts.

[EDITOR'S NOTE.—We are aware that the finest dust obtained in wood-working factories is an industrial hazard, and like most other dusts can create explosions. Flour, for example, was the cause, some 20 years ago, of one of the most disastrous explosions in the U.S.A. It can, of course, be air-separated in the normal collecting chambers, but the hazard is always present. We rather lean to the view that chemical research rather than the plastics moulding industry will solve the problem. However, when some courageous person will attempt the binding of such a dust with a small quantity of plastic binder, he will, as Mr. Blewett says, rid the industry of a nuisance. This, however, is technical research and costly research at that. If only the wood-working industry collaborated and spent some money, we believe it would get results.]

The Case for Carbide

It may be, as Dr. Harry Barron says, that, for lack of any technical representation, Parliament could not possibly appreciate the significance of a carbide industry, but there were certain Members of Parliament who were well informed on this matter. At the outbreak of the war I was requested by friends who had been asked to finance a carbide manufacturing scheme for an opinion on the project. The estimates, specifications and drawings had been expertly prepared and detailed to an extent not usually met with in such projects. Carbide supplies were continuing from Norway, the loss of Malaya and the Dutch East Indies was not generally envisaged, and it was remembered that a carbide manufacturing plant which was established in Manchester during the last war had to close down after the war owing to the competition of cheaper imported material. Failing some measure of support or encouragement, therefore, from the Government and from users of carbide, for existing and projected applications, there was little incentive for private investors in such a venture.

S. R. DEVLIN,
CATALIN, LTD.

I have read your plea with interest, and also Dr. Harry Barron's supporting letter, and the facts are that the case for carbide has never been established commercially.

The manufacture of carbide before the war was governed by economic considerations, and any development during the war must of necessity be regarded as a war-time measure.

I can state that the question of producing carbide has often been considered in this country, and I can assure you that the hands of the " Political Racketeers " are quite clean in respect to carbide.

The reasons were geographical—in Scandinavia they can produce by means of water power one electrical horse-power at half the cost to produce here the equivalent horse-power by the aid of coal. Therefore, to invest half a million pounds in plant to produce carbide that could be imported at one-half the price was not a proposition.

In Germany, however, the production of carbide was an economic one, in precisely the same way as it may become one here as a war-time or after-war measure.

You cite the hydrogenation of coal as a wise example and also as a testimony to Government foresight. I fail completely to appreciate the wisdom of continuing a process that consumes an enormous subsidy, that never will—nor ever can—pay a dividend as it costs four times as much to produce one gallon of petrol in comparison to the cost of cracking from crude petroleum, and this does not take into account the tremendous advantages to be gained by hydrogenation of crude oil.

Indeed, bad as that is, there is worse to follow—all the most valuable coal tar products such as the phenols (so valuable to the development of the plastics industry) are lost in the process.

I do think that it is important to recite the facts. HORATIO W. HUTTON.

[EDITOR'S NOTE.—Mr. Hutton has not read our editorials on this subject as carefully as we should wish. We wanted a carbide plant as an insurance against bad times, in fact, against war, and as a training ground for chemical and plastics production. Pre-war economics do not enter into the question except in so far as it affects investors, as Mr. Devlin points out. Our point is that it should have been a Government subsidized concern. Our dyestuffs industry was subsidized and was successful. Our coal hydrogenation plant is subsidized and may be economically unsuccessful, but it has saved many ships and, what is more important, sailors' lives. That is all we care about in war-time. Half a million is a fleabite now.

As for plastics and synthetic rubber the price of raw carbide matters nothing at all. Already chemistry and chemical engineering have lowered the price of synthetic rubber even though carbide has probably increased in price.

Just to complicate the argument, we are willing to bet a large sum to a small one that there is a carbide plant working full out somewhere in the country.]

PRODUCTION NEWS

Raw Materials, New Plant, Works Organization, Control Apparatus, Research, Personal and Trade Notes

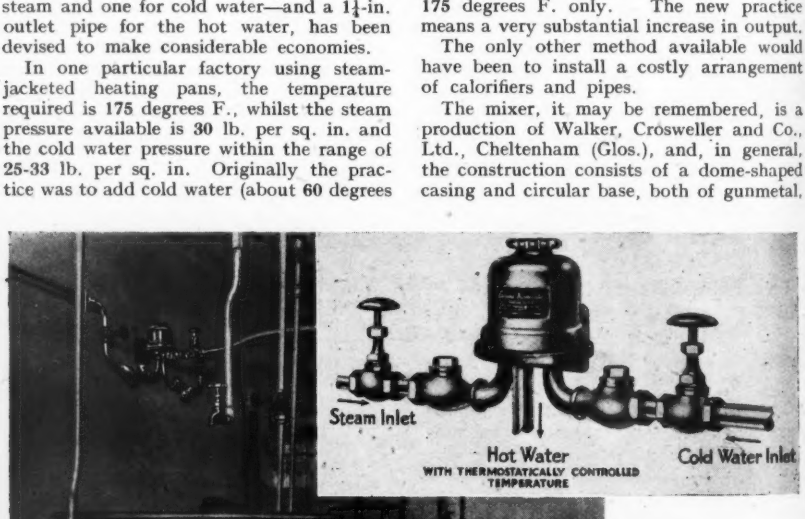
HEATING PANS AND THERMOSTATIC CONTROL.—The general method adopted when using steam-jacketed boiling pans is to fill them with cold water and then heat the latter up to the desired temperature by means of the steam jacket, after which the necessary products are added. This, however, is an unscientific principle, because there is no appreciable circulation in the water, and a considerable waste of time results because of slow heating. A much better method is to supply the hot water direct at the desired temperature. The "Leonard-Thermostatic Type DS" steam and cold water mixer, which has two 1-in. inlet pipes—one for steam and one for cold water—and a 1¼-in. outlet pipe for the hot water, has been devised to make considerable economies.

In one particular factory using steam-jacketed heating pans, the temperature required is 175 degrees F., whilst the steam pressure available is 30 lb. per sq. in. and the cold water pressure within the range of 25-33 lb. per sq. in. Originally the practice was to add cold water (about 60 degrees F.) to the pans and then to heat them up with steam in the jacket; this took about 20 minutes to reach the temperature of 175 degrees F., the temperature afterwards being raised to the boiling point.

However, a live steam and cold water mixer of the above make was installed and the pans, 20 gallons in capacity, are now filled direct from the mixer with hot water at 175 degrees F., which takes four minutes; another four minutes is required to heat the contents of the pan to the boiling point. Thus the whole process from the commencement to the actual boiling point takes only eight minutes, as compared with the previous 20 minutes to heat the water to 175 degrees F. only. The new practice means a very substantial increase in output.

The only other method available would have been to install a costly arrangement of calorifiers and pipes.

The mixer, it may be remembered, is a production of Walker, Crosweller and Co., Ltd., Cheltenham (Glos.), and, in general, the construction consists of a dome-shaped casing and circular base, both of gunmetal,



Leonard thermostatic control for the heating of pans by steam and cold water mixer.

with a horizontal knurled control or hand-wheel to alter the temperature of the hot water as desired. In the base are the two inlet pipes for steam and hot water, having non-return valves and the discharge pipe for the hot water with valve control. Each of the inlet pipes leads to a rotary valve of manganese bronze, with nickel-silver sleeve, operating horizontally, closing or unclosing inlet ports, being operated by two heavy bi-metal strip coils formed of two non-corrodible alloys. These coils operate together as a single unit, and as the temperature of the heated water varies the coils automatically close the cold water inlet and correspondingly open the steam inlet, or vice versa, keeping the outlet temperature steady within a few degrees F., irrespective of variation in pressure and temperature of the water and the steam. Also, this temperature of the discharged hot water is controlled, as stated, by moving the knurled handwheel, which fits over a bush in such a manner that the rotary valves and the thermostatic coils are moved into a new position in relation to the inlet ports, which alters the thermostatically maintained temperature accordingly.

The basic principle is the same as the firm's other thermostatically controlled valves, all of which are suitable for mixing either steam or very hot water with cold water, but differ as regards their output.

PLASTICS CUTTING TOOLS.—The development of plastics for new applications often entails machining, turning, milling, drilling or shaping operations. Many plastics contain materials which attack or erode the cutting tool, resulting in premature failure of the cutting edge. Various metal alloys have been developed for cutting tools which have proved highly efficient, not only on metals, but also plastics; amongst these are the Colmonoy alloys.

These hard alloys consist of chromium boride crystals, either in a matrix or softer material, or in solid solution. All these alloys have great resistance to all forms of wear and abrasion.

A special grade, Colmonoy No. 9, has been developed for cutting tools. Experiments are at present being carried out to determine the exact increase in life, as compared with other metal alloys. So far it has proved superior to all alloys except those basically of tungsten carbide.

Colmonoy No. 9 is supplied to the consumer in the form of a welding rod. The rod is used with the oxy-acetylene blowpipe to build up the tool to the desired shape, allowing sufficient surplus to grind the tool to size.

The alloy when deposited is hard and does not require hardening or tempering. A tool so treated will keep its edge up to 600 degrees C. The cost of applying Colmonoy No. 9 is approximately 6s. 6d. per cubic in., so that for a tool with a tip having an insert of Colmonoy $\frac{1}{4}$ in. by $\frac{1}{4}$ in. by $\frac{1}{4}$ in. thick, the cost would be 3d., including the cost of labour.

The time required would be 2 to 3 mins., chiefly taken up in pre-heating the tool to the correct temperature, 600 degrees C. When the tool reaches this temperature Colmonoy is melted on to it with the blowpipe. The melting point of Colmonoy No. 9 is 1,000-1,100 degrees C. The Colmonoy will immediately bond directly on to the tool and " tin " the surface. The tool can then be built up to the desired shape by adding more Colmonoy. This work is carried out satisfactorily by the average welder, after half an hour's tuition.

Other Colmonoy alloys are available for building up worn parts such as shafts, mixer blades, swing hammers, chains, sprockets, cams, plungers, press tools, forming tools, etc. Different grades are available for application by the electric arc and carbon arc welding, as well as by oxy-acetylene welding.

Colmonoy alloys are manufactured by the Wall Colmonoy Corporation of Detroit, who are represented in this country by Messrs. A. S. Young and Co., Ltd., of " Tower " Works, Woodside Lane, North Finchley, N.12. Messrs. A. S. Young and Co., Ltd., are in a position to carry out experimental work connected with applications of Colmonoy alloys to plastic moulds or machine tools, in their laboratories, and can also give the necessary tuition to users wishing to use Colmonoy alloys in their works.

CLOTHING COUPONS FOR THE PLASTICS INDUSTRY.—Following application by a committee of the British Plastics Federation to the Board of Trade for the provision of extra coupons to various processes, the Board of Trade have agreed to receive applications from employers of workers in the plastics industry.

In view of the special conditions in this industry, the distribution of coupons will not be made in the normal way through the Ministry of Labour and National Service, but by the Board of Trade. By arrangement between the Engineering and Allied Employers' Federation and the British Plastics Federation, employers who are

members of both organizations or who are members of the British Plastics Federation only, or who are not members of either organization, should make application through the British Plastics Federation. Employers who are members only of the Engineering and Allied Employers' Federation should make application through that organization.

A schedule of coupon allowances has been devised and circulated:—

25 Extra Coupons

Process worker—mixers, millmen, still operators, cast resin operators, sifters, grinders, weighers, pelleters, granulating, densifying, rolling.

Hydraulic and power press moulders.

Operator in formalin seasoning room.

20 Extra Coupons

Maintenance fitter wholly engaged in maintaining plant producing plastics.

15 Extra Coupons

Cementer, cellulose sprayer; sheet cleaner (metal or plastics); slicing machine operator; seasoning stover; scrap soaker.

10 Extra Coupons

Maintenance electrician; tool fitter wholly employed in plastics production shop.

THE GOVERNMENT AND PLASTIC CUPS.—In view of the shortage of china and crockery, Mr. W. W. Wakefield, M.P. for Swindon, asked Captain Waterhouse, Parliamentary Secretary to the Board of Trade, whether "plastic or other substitute raw materials would be used." Captain Waterhouse replied: "The possibility of increasing the production of plastic tableware is being examined in consultation with the Ministry of Supply and the industry. Manufacturers of articles of plastic material are heavily engaged, however, on important Government work, and they can make only a relatively small contribution to our total requirements of crockery."

TRANSACTIONS OF THE INSTITUTE.—We have received the June, 1942, issue of the "Transactions of the Institute of the Plastics Industry," which has just been published. It contains the papers that have been read before the Institute during the past year, and includes "Debate on the Plastics Industry," which was opened by Mr. A. G. Snell before the Midland Section; "War and the Plastics Industry," by T. L. Birrell, M.A.; "Plant for Injection Moulding, Die-casting and Extrusion," by J. L. Daniels, B.Sc.; "Plastics in Aircraft," by J. D. North; "The Plastics Industry," by Major S. M. Mohr, O.B.E., M.C.

INFRA-RED DRYING.—The use of infra-red radiation for drying has developed considerably in the United States for the rapid drying of paints, lacquers and other films. The speeding up of drying has been applied to adhesive cements and more recently to the drying of timber. One report states that timber 1 in. thick can be dried in little more than half an hour, whereas normal kiln drying takes three days.

MOTORCAR OPERATING COSTS.—Accepted, for many years, by thousands of commercial-vehicle operators as a standard work on costing, a new and up-to-date edition of the Tables of Operating Costs, compiled by "The Commercial Motor," has just been published. It appears at a time when the problem of costs is not merely an individual consideration, but has also a national significance, and as the Tables take due account of war-time increases they comprise a completely trustworthy guide to present-day operations.

The Tables, of which there are 21, are each divided into two sections, one giving costs and the other charges—the latter being of invaluable assistance to hauliers in the case of goods vehicles, and the operators in the case of buses, coaches and hire cars. The statistics are unusually comprehensive, and cover all types of commercial vehicle, whether the fuel used be petrol, oil, producer gas, steam or electricity.

The Tables of Costs are based upon the experience of a large number of operators, and, accordingly, are average figures, but they have a direct applicability in many spheres of commercial-motor use; where conditions are better or worse than those normally met it is a simple matter to make appropriate adjustments.

This is the 32nd year of publication of the Tables, which are acknowledged throughout the road-transport industry, as well as by the railways and many Government Departments, to be the most accurate analysis of costs for commercial vehicles of all types that is available. The new edition sells at 2s. 2d., including postage, and may be obtained from Temple Press Ltd., Bowling Green Lane, London, E.C.1, or from all leading booksellers at 2s.

The fact that goods made of raw materials in short supply because of war conditions are advertised in this journal should not be taken as an indication that they are necessarily available for export.

Resinoids and Other Plastics as Film Formers

By B. J. BRAJNIKOFF,
Consulting Electrical Engineer

VIII.—Industrial Synthesis of Styrene

THE progress in plastics development has been markedly accelerated by coming into prominence of the new synthetic resin derived from styrene or vinyl benzene. Since these resinoids, $CH_2=CH.C_6H_5$, are polymers of the vinyl benzene, they belong, therefore, to the vinyl or ethenoid series, and are very closely related to polyvinyl chlorides.

The first record of the ability of styrene to polymerize dates back as far as 1839, when Simon,[48] in a published account on his experiments, revealed that, under the influence of "air and heat," styrol is transformed into a tough, gelatinous mass.

Notwithstanding, however, the century-old discovery of the polymerizability of styrene, its practical significance, like that of vinyl chloride, was grasped only during the last decade or so, chiefly due to the manifestation by styrol polymers of exceptionally valuable dielectric properties (particularly in connection with high-frequency insulation problems), and the splendid heat/pressure mouldability as well as film-forming qualities. They give mechanically strong, transparent, water-clear resins distinguished by the great chemical inertness and almost complete insensitivity to water.

It will be seen, therefore, that the foregoing outstanding features of polystyrene, unsurpassed by any other type of resinoids, render it an extremely useful plastic, which, in addition to immense potentialities in the insulation field, have far-reaching prospects of technical utilization in the most diverse industries, offering substitutes for such substances as shellac, condenser mica, amber, ebonite, and a number of other scarce or imported materials.

Since the production of a synthetic resin involves two main processes, namely, the preparation of monomeric raw materials and their conversion into a final polymeric product, it follows that the whole survey of styrene may conveniently be dealt with under two headings: (1) Synthesis of Styrene, which is treated in the present section, and (2) The Polymerization Technique that will form the next part of this work.

The Basis of Styrene Synthesis

The application of polystyrene as an industrial plastic material had been proposed in 1916 by Dr. Ostromislensky,[49] the then chief chemist at the Rubber Works "Giant," in Moscow, where his researches resulted in the development of many interesting synthetics, such as cuprene chlorides and others.

However, it is only now that styrene resins are beginning to appear in large quantities on the market under various trade names, e.g., Distrene, Plastoresin, Victron, Resoglaz, etc., to the makers of which belong a large proportion of patented processes for the synthesis and polymerization of styrol.

Nevertheless, despite copious literature on styrene, there are no direct indications as to the methods and technique to be applied in the production of styrene and its polymers.

As a result of the pyrogenic decomposition of many organic substances, styrene is found in gaseous and liquid products of the pyrolysis of coals,[50] and also among the compounds resulting from cracking of petroleum and certain natural and industrial gases.[51]

Since, however, the styrene content in the above products is not large, and its release in a pure state is difficult, preference is given to the synthetic methods of

styrene manufacture, based upon discrete individual compounds. Among them the first place belongs to acetylene, which, according to a number of investigators, can be a serviceable material for production. Thus Berthelot[52] indicated that thermo-polymerization of acetylene at the temperatures over 640 degrees C. yields a mixture of products containing up to 20 per cent. of styrene. The latest researches confirm that acetylene provides a valuable basic material for synthesis, for, according to Dykstra,[53] under certain conditions, styrene may be formed in considerable quantities by polymerizing monovinyl acetylene, which, in turn, may be easily produced by bimerization of acetylene in the presence of copper chloride:—

$$\underset{\text{(acetylene)}}{CH{\equiv}CH} \longrightarrow \underset{\text{(vinyl acetylene)}}{CH{\equiv}C.CH{=}CH_2} \longrightarrow \underset{\text{(styrene)}}{\longrightarrow C_6H_5.CH{=}CH_2}.$$

On the other hand, styrene can be derived by the dehydration of vinyl cyclohexane, i.e., a dimer of divinyl, according to the scheme:—

$$4\ (2CH_2{=}CH.CH{=}CH_2) \longrightarrow C_6H_9.CH{=}CH_2 \longrightarrow C_6H_5.CH{=}CH_2 + 2H_2.$$

It must be borne in mind, however, that both vinyl acetylene and divinyl are raw materials required for synthesis of chloroprene and butadiene rubbers, whereas styrene is also obtainable from different sources; moreover, styrene yields from the aforesaid schemes are not high.

The latter aspect is explained by the circumstance that when styrene is derived from unsaturated aliphatic hydrocarbons as raw materials the reaction may proceed not only with the formation of aromatic nuclei but also in other directions not leading to styrene. On the other hand, dehydrogenation of vinyl cyclohexane, simultaneously with the formation of benzene nuclei, may promote hydrogenation of the vinyl group. For this reason preference should be given to those methods of styrene synthesis which are based on the treatment of easily accessible aromatic hydrocarbons, since in so far as they already contain a benzene nucleus in the molecule, the problem of synthesis is reduced to the formation of the vinyl group.

Such methods include Ostromislensky's[54] earliest processes for producing styrene or its homologues from (a) aromatic hydrocarbons, and (b) by the pyrogenic decomposition of cinnamic acid, which, in turn, is obtainable synthetically from toluol according to the reaction:

$$C_6H_5.CH_3 \longrightarrow C_6H_5.CHO \longrightarrow C_6H_5.CH = CH.COOH \longrightarrow C_6H_5.CH{=}CH_2.$$

By means of carboxylation, cinnamic acid forms styrene in the following manner[55]:—

$$C_6H_5.CH = CH.COOH \longrightarrow C_6H_5.CH = CH_2 + CO_2.$$

In his improved process (c) for the manufacture of styrene, Ostromislensky disclosed that, instead of cinnamic acid, its various homologues, viz., ortho- and para-methyl cinnamic acid may be similarly used, with the direct yield (35 to 45 per cent.) of pure styrol, subject to the temperature at which the process is carried out.

Styrene can also be prepared from cinnamic acid by means of an additive reaction with hydrogen bromide and carbon dioxide, on heating with soda solution[56]:—

$$C_6H_5.CH{=}CH.COOH + HBr \longrightarrow C_6H_5.CHBr.CH_2.COOH \longrightarrow C_6H_5.CH{=}CH_2 + HBr + CO_2.$$

However, the high price of cinnamic acid and rather limited yields of styrene are the drawbacks of the method, for which reason it is unlikely to gain a widespread application in industry.

Phenylethyl Alcohols

Another way of synthesizing styrene consists of splitting off water from α- and β-oxyethyl alcohols or hydrogenhalide from ethylhalide derivatives of benzol.

Of these methods the primary consideration should be given to the process for producing styrene by dehydration of α- or β-phenylethyl alcohols.

The behaviour of both alcohols in this respect is distinctly different. Thus, in the case of α-phenylethyl alcohol (methylphenylcarbinol), the dehydration of which can also be effected in the vapour phase, alkaline catalysts are unsuitable, and only acid dehydrating agents must be used[57] (e.g., sulphuric, phosphoric, oxalic acids, potassium or sodium sulphates, oxalyl chloride).

On the contrary, β-phenylethyl alcohol (benzylcarbinol) forms styrene only in presence of alkaline catalysts, best of all with the fused caustic potash[58]; no splitting off of the elements of water occurs under the action of oxalic acid on this alcohol, and in the presence of acid and sulpho-acids salts it yields a simple ether. As to the production of phenylethyl alcohols, resort may be made to the Grignard reaction; α-phenylethyl alcohol is readily obtained from $C_6H_5.CHO$ and $CH_3.MgI$, or from $C_6H_5.MgBr_2$ and CH_3CHO[59], and β-phenylethyl alcohol—from the chlorhydrin of glycol or ethylene oxide magnesiumbromphenyl[60]. Besides this, α-phenyl alcohol may be derived by deoxidizing acetophenone with sodium amalgam[61] and β-phenyl alcohol — by reducing ethyl ether of phenlyacetic acid.[62]

The preparation of styrene from acetophenone can also be accomplished by the action of zinc amalgam and hydrochloric acid.[63] Under the action of acetylene on benzol, in presence of aluminium chloride, the reaction results in a mixture of various products, including styrene, but its yield is rather moderate.[64]

Production of Ethylbenzol

The principal raw material for making styrene by the methylphenlycarbinol method is ethylbenzol, which can be produced from the reaction of Friedel and Kraft; that is, by the action of ethyl bromide or ethyl chloride on benzol in presence of aluminium chloride.[65] Very efficient processes for obtaining ethylbenzol have lately been developed by simplifying the procedure of condensing benzol with ethyl chloride catalysed by aluminium chloride,[66] or with ethylene,[67] as well as by means of the destructive dehydrogenation of naphthalene;[68] in order to obtain carbinol from ethylbenzol the latter is subjected to chlorination (via molecules containing a suitable side-chain), and the derived chloride is then saponified. Thus, the entire synthesis may be represented by the following scheme:—

$$C_6H_6 \xrightarrow{+Cl_2} C_6H_5-C_2H_5 \xrightarrow{+H_2O} C_6H_5CHCl.CH_3 \xrightarrow{} C_6H_5CHOH.CH_3 \xrightarrow{-H_2O} C_6H_5.CH=CH_2$$

This method has been elaborated by Professor Zalkind[66] and his co-workers in the Russian Institute of Plastics and has already proved its industrial worth after several years of semi-scale experimental trial.

Alternatively, by introducing two atoms of bromine, with the subsequent treatment by magnesium:

$$C_6H_5.CH_2.CH_3 \longrightarrow C_6H_5.CHBr.CH_2BR \longrightarrow C_6H_5.CH=CH_2$$

Lastly, styrene can be produced by pyrogenic dehydrogenation of ethylbenzene: $C_6H_5.CH_2.CH_3 \longrightarrow H_2 + C_6H_5.CH=CH_2$.

With regard to chlorination of ethylbenzene the available data contains numerous variants: α-chlorethylbenzene is derivable under the action of chlorine in the cold, in sunlight, as well as by chlorinating at relatively moderate temperature range (20 degrees to 120 degrees C.).[69]

The action of chlorine on boiling in diffused light results also in, mainly, α—chlorethylbenzene, with a small admixture of β-derivative. According to other data, the principal product formed on boiling is β-chlorethylbenzene. To split off the elements of hydrogenchloride, it has been proposed to pass the vapours of chlorethylbenzene through a tube heated up to 600 degrees to 750 degrees C. over suitable catalytic agents (e.g., activated carbon, bauxite, oxides of iron, aluminium, nickel, zinc, copper, etc.),[70], or in their absence.[71]

Chlorethylbenzene may also be treated in the liquid phase by different reagents: nitrogen organic compounds (pyridine, quinoline, dibenzylamine, aniline)[72]; mineral or organic acids, which should be less volatile than hydrochloric acid, for example, phosphoric, sulphuric, palmitic, benzoic, monochloracetic, and others;[73] or salts of mercury or zinc (viz., mercury chloride, mercury sulphate, zinc chloride).[74]

Both α- and β-dibromethylbenzene are derived from ethylbenzene under the action of bromine at 145 degrees to 150 degrees C.,[75] and the splitting off of bromine is effected by the magnesium in ether solution.

Finally, dehydrogenation process of ethylbenzene consists of subjecting its vapours to the action of heat at a high temperature range (500 degrees to 800 degrees C.), either in presence of catalysts,[76] or without their aid.[77] The catalytic substances suitable for the purpose are difficultly reducible oxides of metals and their compounds, carbon, silica gel, mixtures of copper, iron and nickel on pumice stone, etc.

Styrene is obtained in admixture with the unchanged ethylbenzene, and the liberation of the product in a pure state may be effected by applying a low-temperature cooling,[78] whereby styrene is crystallized out.

Catalytic Dehydrogenation of Ethylbenzene into Styrene

A successful reaction of dehydrogenating of ethylbenzene should, of course, be one of the simplest and most convenient means for passing to styrene. This reaction has been known for a long time. In 1867 Berthelot[79] had established that the passage of ethylbenzene through a porcelain tube kept at red heat induces the splitting off of hydrogen, with the formation of a mixture containing up to 30 per cent. of styrene.

However, these experiments have shown that the phenomena of pyrogenic decomposition of ethylbenzene are exceedingly complex, giving rise, apart from styrene, to numerous other products, among which are found benzene, ethylene, toluol, naphthalene, etc. The patent literature testifies that appreciably better results are obtained through application of selective catalysts accelerating the dehydrogenation and averting thereby the occurrence of the further decomposition processes.

A notable contribution to the detailed study of the methods for styrene synthesis has been made by the researches extending over the past decade in Russia. A number of workers led by Zalkind[66] in the Russian Institute of Plastics succeeded in the dehydrogenation of ethylbenzene to styrene in a simple and economic manner.

In 1940, an improved process for catalytic dehydrogenation of ethylbenzene and polyethylbenzene (in CO_2 medium) into polymerizable substances was evolved in the Russian Academy of Sciences, and at present work is being intensified at the Laboratory of Super-High Pressures under the guidance of the Academician Zelinsky, in synthesizing from vinyl acetylene alcohols and their alkenyl esters the analogues of styrene, with the aim of deriving new allene-diene compounds related to the series of rubber-like plastics.

According to Zalkind,[66] ethylbenzene can be made from benzene and ethyl chloride with the yield of 75 per cent. of the theoretically possible, by heating the components in the presence of aluminium chloride, whereby the products of ethylation of benzene with a higher boiling range may also, in considerable proportion, be converted into ethylbenzene by heating them with benzene and aluminium chloride.

The same investigators also found that α-chlorethylbenzene is easily saponified by an aqueous soda solution, with the formation of methylphenylcarbinol. Accordingly, it has become possible to pass to styrene not only through splitting off of hydrogen chloride, but by a saponifying operation, with the subsequent dehydrogenation of methylphenylcarbinol. Hence, the task that the above workers had to tackle extended to the study of the detailed conditions of the

following reactions: (i) the production of ethylbenzene, (ii) its chlorination with the object of deriving α-chlorethylbenzene, (iii) splitting off from the latter of the elements of hydrogen chloride, (iv) obtaining methylphenylcarbinol by saponification of α-chlorethylbenzene, and (v) dehydrogenation of methylphenylcarbinol.

In this way Zalkind and his school have actually worked out two methods for producing styrene from chlorethylbenzene: (a) by the direct splitting off of elements of hydrogen chloride, and alternatively (b) by the saponifying of methylphenylcarbinol and dehydrogenating the latter. Owing to the relatively high cost and scarcity of quinoline, as catalyst, the second method was considered to be more advantageous and accepted by the Russian Institute of Plastics for the exploitation in an experimental factory. It should be mentioned, however, that experience gained later showed that pure quinoline may be effectively replaced by those quinoline bases which are readily available as a by-product of coke works.

Chlorination of Ethylbenzene

Chlorethylbenzene can be obtained with the yield up to 90 per cent. from ethylbenzene by chlorinating the latter in presence of the phosphorus pentachloride, until the gain in weight reaches 60 per cent. of the theoretical, after which chloride may be separated out from unreacted hydrocarbons and polychlorides by distillation in vacuo. Saponification of the chloride is best accomplished by heating it with 10 to 16 per cent. soda solution, and then distilling the crude carbinol under vacuum. The yield of purified carbinol reaches 90 per cent.

The simplest way to produce styrene from methylphenylcarbinol is to heat this alcohol with a small quantity (3 to 5 per cent. of the weight of carbinol) of potassium bisulphate up to 120 degrees to 200 degrees C. The products of dehydration, i.e., styrene and water, are driven off from the reaction chamber, where they separate into two layers: the top portion is then removed, dried and distilled at reduced pressure, of the order of 30 mm. Hg. in a current of hydrogen, at 55 degrees C.

In consequence of the partial polymerization, the yield of styrene from carbinol did not exceed 75 per cent. of the theoretical amount. Futhermore, it was found that sulphuric acid is an advantageous substitute for potassium bisulphate, resulting in the reduction of the temperature required for dehydrogenation process and increased yield of styrene up to 80 per cent.

On the other hand, a practical verification of certain patents,[80] carried out by Russian plastics technologists, demonstrated that styrene yield from dehydrogenation reaction may be raised to 90 per cent., if the procedure is performed in the vapour phase over aluminium oxide heated up to 380 degrees to 400 degrees C.

Therefore, depending on dehydrogenating method used, the yield of styrene, in its production on the laboratory scale, may fluctuate between 60 and 73 per cent. of the ethylbenzene employed.

Experimental Factory Production

The synthesis scheme for making styrene on a semi-industrial scale comprised the derivation of chlorethylbenzene by the method as described above; this was saponified without preliminary purification from ethylbenzol and polychlorides by distillation. Ethylbenzol was then released from the saponification products by distilling in vacuo, giving methylphenylcarbinol, much contaminated with various impurities. The next operation was the dehydrogenation of the crude carbinol catalysed either by potassium bisulphate or sulphuric acid, and the raw styrene, thus derived, was subjected to rectification at a reduced pressure of about 20-30 mm. Hg. The yield of the resultant styrol, containing up to 5 per cent. of foreign matter, does not exceed 55 per cent. calculated from the ethylbenzene employed.

Thus, it will be seen from the above that this variant of synthesizing styrene from ethylbenzene, comprising five opera-

tions: (i) chlorination, (ii) saponification, (iii) distillation of ethylbenzene, (iv) dehydrogenation of carbinol, and (v) purification of crude styrene, is very complicated and does not give a sufficiently high yield of styrene.

For these reasons the Russian Institute of Plastics decided to verify experimentally another variant of styrene synthesis from ethylbenzene, by means of which styrene is obtained in a form directly suitable for polymerization, from α-chlorethylbenzol by splitting off from the chloride the elements of hydrogen chloride:

$$C_6H_5.C_2H_5 \xrightarrow[-HCl]{+Cl_2} C_6H_5.CHCl.CH_3 \longrightarrow C_6H_5.CH=CH_2$$

Judging by the patent data,[81] this reaction can be effected by heating chloride with organic bases, such as quinoline or pyridene, and also with certain other catalysts. Besides α-halogen alkyl benzol, its β-variety or mixture of the two, catalysed by a minute quantity of inorganic substances (e.g., mercuric oxide, mercurous chloride, mercuric acetate, zinc chloride, and the like), can be decomposed by heat into styrene and hydrogen halide.

Experiments performed by Kohn in the same Institute showed that, on splitting off of hydrogen chloride by quinoline, the yield of styrene from the distilled α-chlorethylbenzol increases to 80 to 85 per cent. of the calculated quantity. Hence, by applying this variant of synthesis, it is possible to produce styrene with the yield up to 77 to 80 per cent. of ethylbenzol used. The yield of styrene is, however, much reduced if chlorethylbenzene not freed from polychlorides by previous distilling is treated with quinoline. On the other hand, the distillation of α-chlorethylbenzol, owing to its instability, is frequently aggravated by a strong resinification reaction even when carrying out the process in glass apparatus and under appreciable vacuum; in such a case the decomposition of chloride is speeded up by the admixture of some impurities, for example, traces of iron. Therefore, the purification of the chloride by distilling may present some processing difficulties in large scale manufacture. In addition, the production of styrene by this method is hampered by an extra operation, viz., the regeneration of a base, which involves an additional expense for reagents (alkali) and requires special supplementary equipment.

Consequently, although this method gives higher yields of styrene, it is, despite its apparent simplicity, not less complicated than the process according to the first variant, since it is composed of the following five operations: (i) chlorination of ethylbenzol, (ii) purification of crude chloride by distilling, (iii) heating chloride with bases, (iv) rectification of raw styrene, and (v) regeneration of a base.

As regards the synthesis of styrene from β-phenylethyl alcohol, the reaction of dehydration of this alcohol, as has been disclosed by Sabetay,[82] progresses with exceptional facility, even in the presence of alkali, leading to almost maximum theoretically possible yield. In this respect it differs advantageously from the reaction of dehydration of methylphenylcarbinol, which is accompanied by a partial polymerization of hydrocarbon (with the use of acid catalysts). However, the relatively high-priced β-phenylethyl alcohol hinders the penetration of this method into industrial fields.

As has been proved by experimental studies of Shorygin[83] and others in Russia, this alcohol can be synthesized with the yield up to 70 per cent. of a theoretical amount by the action of ethylene oxide on magnesium - chlorethylbenzene, derived from chlorbenzene and metallic magnesium in the absence of solvent. Simpler still, it can be made by treating benzene with ethylene oxide in the presence of aluminium chloride.[84] Thus, styrene synthesis in this case consists of only two operations: (a) the production of alcohol and (b) its dehydrogenation:

$$C_6H_6 \xrightarrow[-H_2O]{+C_2H_4O} C_6H_5.CH_2CH_2OH \longrightarrow C_6H_5.CH=CH_2.$$

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However, a pure ethylene oxide itself, which is required for this synthesis, in turn, has to be derived from ethylene, and may not always be available. Meanwhile, the necessity for its manufacture may be obviated, without complicating the synthesis of styrene, if the latter is obtained by dehydrogenation:

$$C_6H_6 \xrightarrow{+C_2H_4} C_6H_5.CH_2.CH_3 \xrightarrow{-H_2} C_6H_5.CH = CH_2.$$

Catalysts and Catalytic Fatigue

As is known, styrene is readily formed in appreciable quantities, side by side with other products, by simple pyrolysis of ethylbenzol. Thus, Dobrinsky[85] and others, by passing the vaporized ethylbenzol through a tube heated at 650 degrees C., obtained, together with benzene and toluene, 17 per cent. of styrene. According to other workers,[86] styrene yield from ethylbenzene pyrolysed in an iron tube may exceed 30 per cent., and in presence of dehydrogenating catalysts it is considerably higher.

Suitable catalysts for this reaction, as disclosed by the patent records, are oxides of many metals, for example, aluminium, magnesium, zinc, calcium, cerium, as well as such oxides which, as, for instance, ferric and nickel oxides, in dehydrogenation process are reduced to metal. The reaction is conducted at the temperatures ranging between 500 and 800 degrees C. in vacuo, or by diluting vapours of ethylbenzene by inert gas, or by substances capable of binding hydrogen released by dehydrogenation.[87] By condensing the catalysed vapours of ethylbenzene and then distilling, a product is obtained consisting, essentially, of styrene and ethylbenzene.

Large-scale experiments performed in Russia by Zalkind and Bulavsky[88] demonstrated that using copper oxide (on kieselguhr), or mixture of magnesium and chromium oxides, oxides of aluminium and zinc, as catalysts and conducting the reaction at 620 degrees to 650 degrees C., preferably in vacuo, it is possible to obtain styrene with yield up to 70 to 80 per cent. estimated on the basis of ethylbenzene used.

Recent research by Stenberg's group in the same Institute of Plastics showed, however, that dehydrogenating catalysts lose, with time, their effect, owing to deposition of a coke layer; it was also discovered that this " catalytic fatigue " can be partly or totally removed by burning out the coke film deposited on the catalytic substance, thereby restoring its ability to function.

Thus, a catalyst, which, at the start of dehydrogenation, at 625 degrees C. and 75 mm. Hg., was giving the condensate containing 75 per cent. of styrene, and whose capacity after 11 hours' work dropped to half, regained after second regeneration (after functioning for 20 hours), 95 per cent. of its original activity.

On the other hand, it has been found that, although the variation of pressure from 50 mm. to 300 mm. Hg has little effect on the styrene yield, the elevation of pressure to the atmospheric level reduces the amount of the final product.

With regard to separation out of pure styrene from its mixtures with ethylbenzene, it was shown that it can be easily performed by rectification of condensate in vacuo in a column of adequate height fitted with a dephlegmator;[89] to prevent the polymerization of styrene during the distilling stage, recourse may be made to antioxidants, adding to condensate a fraction of 1 per cent. such substances as, for example, hydrochinone, or, better still, pyrogallol.

Deductions

From systematized data as outlined above, it may be observed that, notwithstanding a large number of methods for styrene synthesis, only a few of them meet the requirements of modern industry. Thus, if we exclude from the afore-described processes, those reactions whereby styrene is formed in poor quantities, together with many other products, there remain the methods of styrene synthesis as summarized in the table on the following page.

Methods of Styrene Synthesis of Industrial Importance.

Raw materials	Intermediate products	Characteristics of method
(i) Ethyl alcohol	Divinyl, vinylcyclohexene	Yields of styrene are not high, raw materials find other applications. Processes are not sufficiently developed
(ii) Carbide of calcium ..	Acetylene, vinylacetylene	
(iii) Toluene and acetic anhydride	Benzaldehyde and acetic acid	Styrol yields are not large. Method is not economical
(iv) Benzene and ethylene oxide	Chlorbenzene, β-phenylethyl alcohol	High yield of styrene. Process is applicable, if a cheap ethylene oxide is available
(v) Benzene and ethylene oxide	β-phenylethyl alcohol	
(vi) Benzene and ethylene (or naphthalene)	Ethylbenzene, chlorethylbenzene, methylphenylcarbinol	Technique of the method is well established, raw materials are abundant, but the production scheme is complicated and yields of styrol are moderate
(vii) Benzene and ethylene (or naphthalene)	Ethylbenzene, chlorethylbenzene	
(viii) Benzene and ethylene (or naphthalene)	Ethylbenzene	High styrene yield, raw materials are readily available and the method of manufacture is simple and efficient

Conclusions

It will be seen from this summary that at present only by utilizing methods of styrene synthesis from ethylbenzene, the manufacturer of styrene may expect the assured continuity of supply of relatively cheap raw materials. Yet the elaborate processes (vi) and (vii) based upon the convertion of ethylbenzene into α-chlorethylbenzene, give rather moderate yields of styrol. The last method (viii) based upon dehydrogenation of ethylbenzene, obviously, merits the greatest attention, since styrene synthesis by this procedure is characterized by simplicity, labour economy, and the minimum expenditure for auxiliary reagents, thus affording effectual means for producing styrol with high yields.

(To be continued)

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